

NASA TT F-10,227

ORGANIC SEMICONDUCTORS

C. Hamann

FACILITY FORM 602	N66 33683	
	(ACCESSION NUMBER)	(THRU)
	75	1
	(PAGES)	(CODE)
		26
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

Translation of "Organische Halbleiter"
 Physica status solidi, Vol. 12, pp. 483-532, 1965

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) 2.50Microfiche (MF) .75

ff 653 July 65

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
 WASHINGTON
 AUGUST 1966

CONTENTS

	Page
1. Introduction	1
2. Historical Outline	1
3. The Basis of Charge Transport	2
3.1 The system of conjugated double bonds	2
3.2 The crystal structure	5
4. Theory of Charge Transport	6
4.1 The electron gas model	6
4.2 The tunnel effect	8
4.3 The bands model	9
4.4 The hopping process	11
4.5 Ionization and exciton dissociation	12
5. Classes of Materials	13
5.1 Polycyclic aromatics and their derivatives	13
5.2 Organic dyes with ion bonding. Triphenyl methane dyes	13
5.3 Halide and alkaline metal complexes	14
5.4 Additive complexes between two organic molecules. Charge transport complexes	15
5.5 Heterocyclic compounds	16
5.6 Natural substances of animal and vegetable origin	16
5.7 Polymers with distinct conjugation system	17
6. Preparation Technique	18
6.1 Purification methods	18
6.2 Chemical and physical analysis	19
6.3 Crystal growth and doping	21
7. Measurement Methods	21
7.1 Contacting method	22
7.1.1 Contacting with set-on metal electrodes	22
7.1.2 Contacting with metal layers	22
7.1.3 Contacting with mercury, pastes, suspensions and electrolytes	22

	Page
7.2 Measurement of conductivity	23
7.3 The measurement of thermal voltage	24
7.4 Measurement of the Hall effect	25
7.5 Photoelectric measuring processes	27
8. Measurement Results	30
8.1 The nature of the charge carrier	30
8.2 The excitation energy of the charge carrier	31
8.3 Concentration and mobility of the charge carrier	38
8.4 Trap concentration and trap depth	45
8.5 The anisotropy of the electric conductivity	47
8.6 Concentration of unpaired spins	49
8.7 Catalytic properties	50
8.8 Molecular substitution lattice defects	50
8.9 Adsorbed gases and vapors	51
9. Possible Applications of Organic Semiconductors	53
9.1 Organic photodiodes and photocells	53
9.2 Organic rectifiers	54
9.3 Thermoelectric structural elements and other possibilities for use	54
10. The Importance of the Research Field and its Future	55
References	56
Supplement to the Bibliography	64

ORGANIC SEMICONDUCTORS

C. Hamann

33683

1. Introduction

The study of the semiconductor properties of organic solids has become an /484* extensive discipline in solid state physics in recent years. Research has been concentrated on all phenomena that are associated with charge transport in individual molecules and molecular crystals. Because of the practically unlimited number of organic compounds, a wide field has been opened for the synthesis and investigation of semiconducting structures. With the accretion of experimental and theoretical results in the field of semiconductor physics, there has been a number of attempts to open up new areas that enable us to anticipate the use of organic semiconducting compounds for special technical problems. The results increase our knowledge of semiconductor physics in the fields of organic synthesis, structure research and crystallography. There is a spread to related fields such as biochemistry, biophysics and organic catalysis, which should extend still more in the future.

2. Historical Outline

The development of the research is treated in a number of surveys (refs. 1-4b). For this reason only significant stages will be mentioned.

Although the investigation of the semiconductor properties of organic compounds represents a relatively young science, the first works extend back to the turn of the century. In 1906 Pocchettino discovered the photoconductivity of anthracene (ref. 5) of which the dark conductivity and spectral sensitivity of the photocurrent were examined in the years 1910 to 1913 (refs. 6 and 7). In the 1930's experiments on the photoconductivity of triphenyl methane dyes were begun (ref. 8) and the amplification of photoemission of alkaline metals by aromatic compounds was discovered (ref. 9).

Szent Györgyi furnished a prologue to works of strongly biophysical character (ref. 10) when he discovered a correlation with energy transfer processes in the living organism from the work on charge transport in organic materials, particularly the photoconductivity of proteins.

In 1941 Vartanyan (ref. 11) began his basic work on dyes, which later /485 led him, independently of Eley (ref. 12), to the discovery of the semiconductor

*Numbers given in margin indicate pagination in original foreign text.

properties of phthalocyanines (ref. 13). At the end of the 1950's polymers (e.g., refs. 14-18) and charge transfer complexes (e.g., refs. 19-23) were drawn into the research and during the years 1959 to 1961, building on measurement techniques and theoretical methods, the works on natural vegetable and animal substances increased (e.g., refs. 24-28).

Kepler, Bierstedt and Merrifield published investigations in this framework relating to TCNQ complexes (ref. 29) which emerged as the organic compounds with the highest conductivity known at the time, namely $100 (\Omega\text{cm})^{-1}$. Recently, by measurements of thermal voltages (refs. 30-34), of the Hall effect (refs. 35-39), and by optical methods for determination of carrier mobility (refs. 40 and 41), successful experiments have been undertaken to clarify the conduction mechanism in organic compounds.

These refined and comprehensive measurements have contributed to the concept apparently enunciated by Inokuchi in 1954 which defines "organic semiconductors" and to the indication of its validity for specific organic compounds and whole classes of substances.

3. The Basis of Charge Transport

3.1 The system of conjugated double bonds

In general, organic compounds, depending upon their electrical properties, belong to insulators with specific room temperature conductivity of $\sigma \leq 10^{-14} (\Omega\text{cm})^{-1}$.

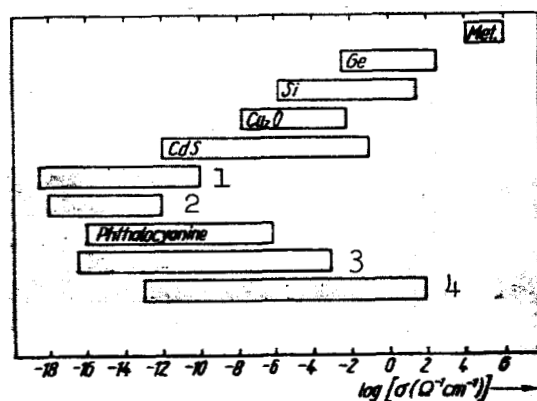


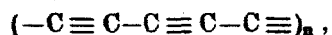
Figure 1. Comparison of the electrical conductivity of inorganic and organic solids.

1, Organic insulator; 2, aromatics; 3, polyacrylnitrile; 4, complex of charge transfer.

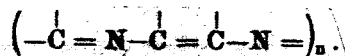
For certain characteristic organic semiconductors figure 1 shows that the conductivity of organic compounds in special cases is more accurately expressed as $\sigma \leq 10 (\Omega\text{cm})^{-1}$. This unusually high conductivity for such substances can be traced back in agreement with the special bond relationships in the individual molecule. The chemical structure of organic semiconductors almost without exception shows a system of conjugated double or triple bonds of the form /486



or



wherein nitrogen, sulfur, phosphorus and other elements can be drawn in as heteroatoms in the conjugation



This characteristic structure and its properties demand close consideration.

In the simplest case the four valence electrons of carbon form four uniform electron clouds which derive from the mixing of a 2s electron and three

2p electrons. These four sp^3 hybrids, together with those other C-atom bonds, enter into electron clouds which are cylinder-symmetrical with reference to the bond axis of the atoms, which leads to free rotatability around the C-C axis.

A second hybrid state consists of three mutually equivalent sp^2 valence hybrids which are arranged as a triangle in one plane and a $2p_z$ electron whose distribution function is in the form of a dumbbell perpendicular to this plane.

If two sp^2 hybrids are joined to a covalent bond, there occurs on the one hand a σ bond with cylinder symmetrical electron distribution, through overlap of

two sp^2 clouds. On the other hand the individual $2p_z$ electron clouds fuse

without losing their symmetrical character. Thus the nodal surface is retained, which separates the positive and negative areas of the wave function. A π bond with an asymmetrical distribution of the electron charge develops, with the resultant rigidity against rotation about the C-C axis. The σ and π bonds together form a double bond. A triple bond is composed of one σ bond and 2 π bonds.

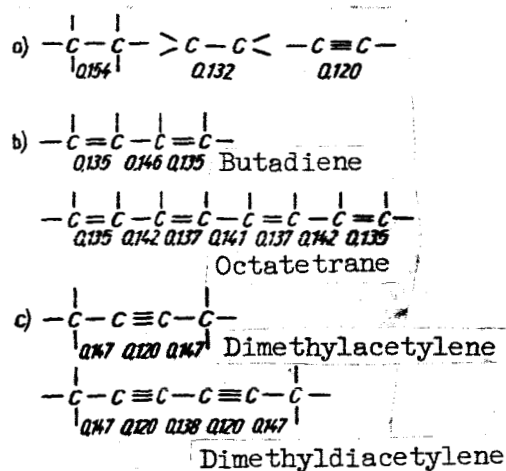


Figure 2. Atom states in conjugation systems: a, isolated bonds; b, conjugated double bonds; c, conjugated triple bonds.

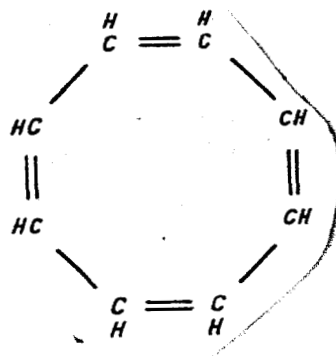


Figure 3. Structure formula of cyclooctatetraene.

In a system of conjugated double or triple bonds, with increasing conjugation the character of the isolated bonds is lost through π electron displacement. This statement is unequivocally supported by measurement of the /487 atom distances (fig. 2). Expanded conjugation systems then have an average C-C bond spacing (e.g., 0.139 nm in a system of conjugated doubled bonds).

Conjugated systems are energetically more stable than nonconjugated equal sum formulas. The occurrence of a π electron cloud particular to a molecule is bound to an even arrangement (polycyclic aromatics are coplanar in an expansion of the molecule by 0.1 nm to ± 1 pm. If the possibility is lacking for coplanarity as in cyclooctatetraene (fig. 3) all the other characteristics of an even conjugated system vanish. An infinitely expanded conjugation system can be treated quantum mechanically like a metal, on the basis of the free mobility

of the π electrons. An approximation of this state is presented by graphite which can be regarded as a highly condensed aromatic compound. An ideally structured conjugation system would have to be superconductive in the direction of the conjugation series. Recently, Little (ref. 190) was able to show theoretically that organic superconductors would have to retain their properties even above room temperature.

3.2 The crystal structure

The considerations indicated under 3.1 show that the transition of the charge carrier from the conjugation system of one molecule to another must be of major importance for the development of semiconductor properties. The mechanism of charge transfer is affected substantially by the spatial interrelationships of the molecules.

Organic molecular crystals without exception belong to the lower symmetry classes (mostly monoclinic lattices). Their crystal lattices are intricate, and the determination of the crystal class is made additionally difficult because of the complicated structure of the elementary cells. For this reason the crystal structure of only a relatively small number of organic molecular crystals has been determined.

As an example we refer to crystallographic data concerning some phthalocyanines. β -modification phthalocyanine crystals belong to the crystal class

C_{2h}^5 . Table 1 shows the dimensions of elementary cells each consisting of two molecules (ref. 42). Figure 4 gives an impression of the spatial arrangement of the phthalocyanine molecule in the elementary cell of metal-free phthalocyanine. The assumption of this arrangement leads to a maximal approach of 488 molecules adjacent to C atoms of 0.34 nm, i.e., the minimum distance usually set by the Waals forces is obtained. With the approach of the molecules there is a slight overlap of the π electron clouds. Similar relationships exist in other organic molecular crystals.

High molecular compounds are generally amorphous or have a partially crystalline structure. The formation of larger crystal domains is strongly inhibited by the complexity of the bonding forces which are often directed by the pressure of a molecular weight distribution through side chains and cross-linked molecules. Polyacrylonitrile which is important for further observations crystallizes in a hexagonal lattice ($a = b = 0.617$ nm, $c = 0.51$ nm = phase axis $\angle = 120^\circ$) (ref. 43). Most high polymers have monoclinic or triclinic crystal domains. The chain-chain distance, in comparison to those of molecular crystals, is large. The crystal structure of thermal and radiochemical products of polyacrylonitrile and other high polymers is not known.

TABLE 1. DATA CONCERNING ELEMENTARY CELLS OF PHTHALOCYANINE CRYSTALS OF BETA MODIFICATION

Material	Axis length (nm)			Angle β
	a	b	c	
Phthalocyanine	1.985	0.472	1.48	122.25°
Be-Pc	2.12	0.484	1.47	121.0°
Mn-Pc	2.02	0.475	1.51	121.7°
Fe-Pc	2.02	0.477	1.50	121.6°
Co-Pc	2.02	0.477	1.50	121.3°
Ni-Pc	1.99	0.47	1.49	121.9°
Cu-Pc	1.96	0.479	1.46	120.6°
Pt-Pc	2.39	0.381	1.69	129.6°

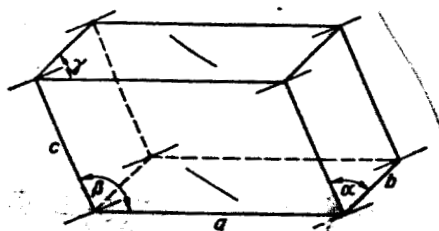


Figure 4. The position of the copper phthalocyanine molecule in the elementary cell of the monoclinic crystal. Intersections between molecular planes and ab planes are drawn in.
 $a = 1.96$ nm; $b = 0.479$ nm;
 $c = 1.46$ nm; $\alpha = \gamma = 90^\circ$; $\beta = 120.6^\circ$. (According to Heilmeyer and Harrison (ref. 39).)

4. Theory of Charge Transport

4.1 The electron gas model

As indicated in 3.1 the π electron cloud in conjugated systems can be ⁴⁸⁸ treated like an electron gas. For a one-dimensional conjugation system the potential will be established as a flat box (refs. 44-46). The periodicity brought about by the lattice can be overlooked because of the screening effect of the electrons.

A system of N π electrons in the one-dimensional case has a length of $a = Nl$ in the x -direction, whereby $l=0.139$ nm must be established. The Schrödinger equation which is independent of time is

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_0\right) \varphi(x) = E \varphi(x) \quad (1)$$

and leads to the energy eigenvalue

$$E_n = n^2 \frac{h^2}{8ma^2} = n^2 \frac{h^2}{8mN^2l^2}$$

The highest occupied level, in consideration of the Pauli principle is

$$E_{N/2} = \left(\frac{N}{2}\right)^2 \frac{h^2}{8mN^2l^2}$$

and the first vacant level is

$$E_{N/2+1} = \left(\frac{N}{2} + 1\right)^2 \frac{h^2}{8mN^2l^2}$$

The calculation results in a lowest excitation level ΔE_1

/489

$$\Delta E_1 = E_{N/2+1} - E_{N/2} = \frac{N+1}{N^2} \frac{h^2}{8ml^2} \quad (2)$$

By a similar calculation there is found for a closed conjugation system hypothesizing a cyclic electron gas

$$\Delta E_1 = \frac{1}{N} \frac{h^2}{4ml^2} \quad (3)$$

where h = Planck's constant and m = electron mass

If there is no complete bond balance in small conjugation systems, the periodic variation of the potential in the potential box can be taken into account by assumption of a sinusoidal potential characteristic (ref. 47). The minima of this potential are in the middle of the shorter bonds. With $V = V_0 \cdot \sin(\pi/l) x$ (V_0 = a few 0.1 eV):

$$\Delta E_1 = V_0 \left(1 - \frac{1}{N}\right) + \frac{h^2}{8ml^2} \frac{N+1}{N^2} \quad (4)$$

The treatment of branched conjugation systems with this model leads to difficulties in calculation. The incorporation of heteroatoms can be accomplished

by a potential pot at the location of the heteroatom. The effect of end groups is taken into account by assumption of an elongated conjugation system. A system of conjugated triple bonds always has a substantially weaker compensation of the bond lengths. V_0 increases sharply. The π electrons are substantially less mobile (ref. 47).

4.2 The tunnel effect

If there are only localized electron states in an organic molecular crystal or amorphous organic solid, electrons can be raised to a vacant level by thermal or photoelectric excitation. Electrons and also holes encounter vacant levels in neighboring molecules, whereby the transition from molecule to molecule can occur by tunneling. With a known potential between adjacent conjugation systems, there is the probability of tunneling and therewith a statement can be made on the mobility of the charge carrier. With the simplified assumption of a potential, there results

$$\begin{aligned} V &= 0, & x < 0, & x > a \\ V &= V_0, & 0 \leq x \leq a \end{aligned}$$

for the permeability of the potential barrier for electrons with energy E

$$D = \frac{16(V-E)}{V^2} e^{-\frac{4\pi a}{h} \sqrt{2m(V-E)}} \quad (5)$$

Eley and Parfitt (ref. 48) using equations (2) and (3) for the dependence of thermal excitation energy of the charge carrier upon the number of π electrons, found a satisfactory agreement with measured values on bonds with predominantly aromatic character. Thereby the statement of the model concerning equality of thermal excitation energy and long wavelength absorption edges is also supported. The values entered in figure 5 for the excitation energies are obtained according to conductivity measurements /490

$$\sigma = \sigma_0 \exp(-\Delta E/2 k T) \quad (6)$$

where σ = conductivity,

σ_0 = preexponential factor,

ΔE = thermal excitation energy,

k = Boltzmann constant, and

T = absolute temperature.

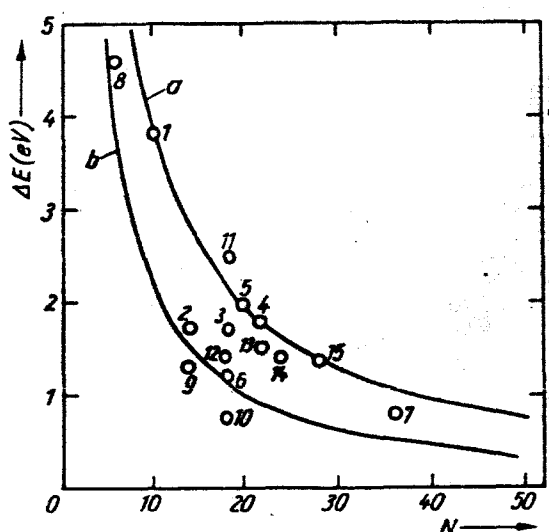


Figure 5. The dependence of thermal activation energy ΔE of the charge carrier upon the number of π electrons N . a, open conjugation system; b, cyclic conjugation system (according to Eley and Parfitt (ref. 48) supplemented according to Meier (ref. 130)); 1, naphthalene; 2, anthracene; 3, naphthacene; 4, pentacene; 5, perylene; 6, p-terphenyl; 7, isoviolanthrone; 8, hydraquinone; 9, chrisoidin; 10, naphthene orange; 11, Bengal rose, 12, methylene blue; 13, orthochrome T; 14, pinacyanol; 15, Victoria blue.

4.3 The bands model

In the case of stronger exchange effect between π electron clouds, certain electron states are dislocated over the entire molecular crystal and spread as bands (fig. 6). While electrons of the inner atomic shell and such as take part in σ bonds present only slightly perturbed energy levels, the π electrons belong to the crystal as a whole. Figure 6 shows the splitting of the discrete molecular spectrum to the band spectrum of the crystal.

At temperature $T = 0$ the valence band is completely occupied and, ^{/491} like the vacant conduction band, it makes no contribution to conductivity. At temperatures $T > 0$, in the case of intrinsic conduction, electrons are raised to the conduction band and holes develop in the valence band. Both kinds of carriers are mobile and contribute to conduction. The electrons follow the Fermi statistics with an apparent occupancy of electron states

$$f(E) = \frac{1}{e^{\frac{E-E_F}{kT}} + 1} \quad (7)$$

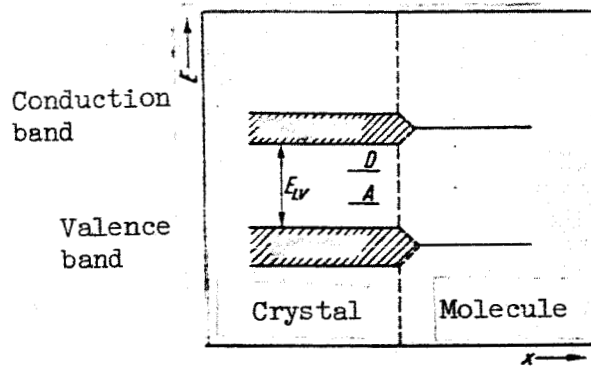


Figure 6. Band energy model:
A, Acceptor level; D, Donor level.

where E_F = Fermi level.

The concentration of the charge carrier n at temperature T is

$$n = \sqrt{N_L N_V} e^{-\frac{E_{LV}}{2kT}} \quad (8)$$

with

$$N_{L,V} = \left(\frac{2\pi m_{n,p}^* kT}{h^2} \right)^{3/2}$$

the effective state density in the valence and conduction band. Here E_{LV} = energy difference between conduction and valence band; and $m_{n,p}^*$ = effective mass of electrons or holes.

Conductivity σ must then satisfy the equation

$$\sigma = en(\mu_n + \mu_p) \quad (9)$$

with mobility μ of the charge carrier.

With structural defects in the crystal and/or foreign molecules (fig. 6) donor or acceptor terms are developed and therewith extrinsic conduction with a thermal excitation energy of the charge carrier $E < E_{LV}$. Usually there are different concentrations of p and n carriers. With sufficiently high

temperature and exhaustion of defects the extrinsic conduction goes over into the intrinsic conduction range.

Equations for the Hall effect and thermal voltage on the basis of the bands model will be given in the following section.

4.4 The hopping process

In recent years the conductive phenomena in semiconductors with extremely low mobility have been theoretically examined (refs. 49 and 50), whereas electric conductivity in semiconductors with high mobility is well summarized in the bands model.

It must be assumed in certain crystals that the charge carrier is trapped in lattice deformations which can be caused by the charge carrier itself. The condition for self trapping is

$$g = 0.035 \frac{E_d m^*/m_0}{C a} > 1; \quad (10)$$

where g = coupling constant with acoustic lattice oscillations,
 E_d = deformation potential,

C = modulus of elasticity,
 a = lattice constant,

m^* = effective mass, and
 m_0 = electron mass.

If $g < 1$, conditions exist which can be comprehended by the concept /492 of dislocated charge carriers. In the case of a strong exchange effect, localized states occur; the charge carriers are fixed in lattice deformations by forces with short radius of influence. The carriers can then jump intermittently through multiphonon processes to the next lattice deformation.

An important distinction in comparison to drift is the lack of Hall effect.

The theoretical treatment substitutes electron-phonon wave packets for pure electron clouds. With nonpolar lattices the band width diminishes to a value of the magnitude of energy indeterminateness of the wave packets through scatter. Here, relaxation time τ is the time during which a charge carrier occupies a seat on the lattice. If τ is large in comparison to the period of lattice oscillations, a lattice perturbation occurs at the occupied spot. If a two phonon process is predicated for charge transport, there is found

$$\mu = \frac{e a^2}{\hbar} \left(\frac{W}{k \Theta} \right)^2 \exp \left(\frac{T}{\Theta} \right); \quad (11)$$

for mobility (ref. 49). Here

a = lattice constant,
 Θ = Debye temperature,
W = band width, and
g = coupling constant.

4.5 Ionization and exciton dissociation

In the corpuscular picture, Riehl (refs. 51 and 52) places a primary act for the existence of a free charge carrier in an organic molecule crystal on the ionization of the individual molecule. For formation of a neighboring ion pair, i.e., for transfer of a π electron to another molecule, energy

$$E = (E_{\text{ion}} - E_{\text{aff}}) - \frac{e^2}{r} \quad (12)$$

is used. Here

E_{ion} = ionization potential of an individual molecule,

E_{aff} = electron addition energy on a neutral atom (electron affinity),

e^2/r = Coulomb energy,

r = intermolecular distance.

Upon separation of an ion pair to a greater distance, we obtain from (12), taking into account the polarizability of the other molecule in the solid,

$$E = (E_{\text{ion}} - E_{\text{aff}}) - \frac{e - 1}{\epsilon} \frac{e^2}{r} \quad (13)$$

(ϵ = dielectric constant).

The concentration of the neighboring ion pair is proportional to $\exp(-E/kT)$, if monomolecular recombination is assumed. This is valid as long as the concentration of the pair is not so high that its average distance comes to the order of magnitude of its extent (ref. 1).

The described mechanism leads to currents that obey Ohm's law. The deviations of a current-voltage proportionality in organic compounds which occur at relatively low field strengths are explained by Northrop and Simpson

(ref. 53) by migration of excitons in exciton bands. Excited states of /493 the individual molecule, which play a role in optical absorption and fluorescence, are propagated in the crystal to exciton bands. They have an excitation energy E_A and they are occupied proportionally to $\exp(-E_A/kT)$. Only

the dissociation of the excitons in an outer electric field leads to the occurrence of free charge carriers and thereby to an increase of conductivity.

5. Classes of Materials

Certain classes of materials have become especially interesting for the study of semiconductor properties of organic substances on the basis of their structure. In most cases only the first overall measurements are available at present, whereby there are as yet no complete classifications of the conduction mechanism, as for instance in the case of the polyacrylonitrile anthracene, phthalocyanine and special complexes.

5.1 Polycyclic aromatics and their derivatives

These compounds are among the first of the organic substances which were studied with reference to semiconduction. Anthracene (fig. 7) as the main representative of this group, has a melting point of 217° to 218° C, is readily soluble in boiling benzene, and is sublimated in a vacuum. The monoclinic crystals can be obtained in dimensions up to a few centimeters in each axial direction.

In addition to anthracene there is a whole spectrum of polycyclic aromatics that are obtainable from coal tar, among them pyrene, coronene and ovalene which present a distinctly parquet-like structure of the conjugation system (fig. 7). Derivatives can be produced by substitution reactions from all aromatic compounds. The variable chemical structure makes possible investigations on the effect of small perturbations in the conjugation system upon the conduction mechanism. As a final consequence, the planes of the graphite lattice built up from a system of aromatic six-member rings can be regarded as highly condensed aromatic compounds.

5.2 Organic dyes with ion bonding. Triphenyl methane dyes

Triphenyl methane constitutes the basic substance of the triphenyl /494 methane dyes such as malachite green, fuchsin and crystal violet, which are mostly present in the form of chlorides. Related compounds are phthaleins such as eosin and erythrosin which must be formulated as salts. The ionic character of the conjugation system has a significant influence on the conduction mechanism. In cationic dye salts an electron is given off to the conjugation system by the substituents. At the same time an absorption band develops in the visible spectrum range and therewith a deepening of color of the complex. Such substituents are in the series with increasing auxochromic effect $--CH_3$, $--OH$, $--OCH_3$, $--NH_2$, $--NHCH_3$, $--N(CH_3)_2$. This effect can be

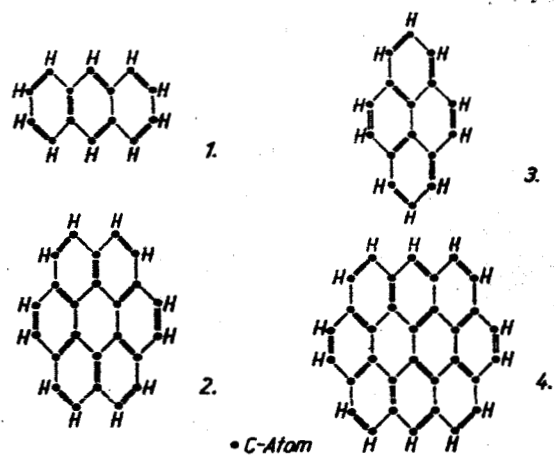


Figure 7. Polycyclic aromatics.
1, Anthracene; 2, Coronene;
3, Pyrene; 4, Ovalene.

explained as an exchange effect of the individual electron pairs of oxygen and nitrogen with neighboring π electrons. In the anionic dye salts the substituents are able to take up electrons from the conjugation system. This property increases in the series

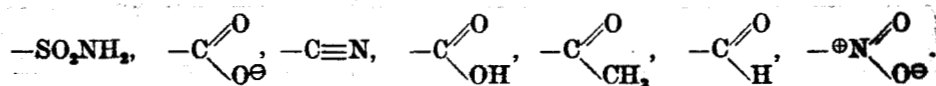
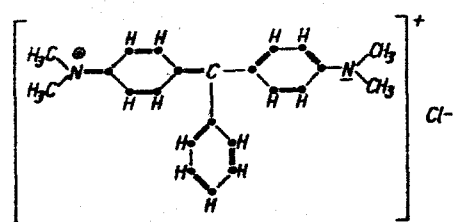


Figure 8 shows examples of an anionic and a cationic organic dye, respectively.

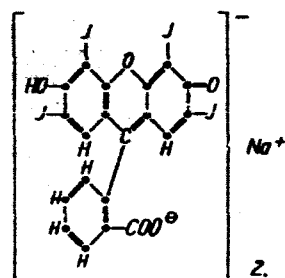
5.3 Halide and alkaline metal complexes

Polycyclic aromatics and their derivatives readily form additive molecular complexes with bromine or iodine (fig. 9). With the introduction of halide to solutions of polycyclic aromatics, deep-colored complexes are formed which /495 are present as 1:1-, 1:2- or 1:3-complexes (aromatic:halide) or as a mixture of such complexes.

To an equal degree, aromatic molecules are capable of acting as electron acceptors, forming complexes with potassium, sodium and lithium, which however are not in stoichiometric proportions. In both cases the role of intermediary of the added halide or alkaline metal atom in charge transport is of great interest. The acceptor or donor properties can be reinforced by the substituents mentioned in section 5.2. The complexes can be obtained in crystalline forms.



1. -C-Atom



2.

Figure 8. Anionic and cationic organic dyes. 1, Malachite green; 2, Erythrosin.

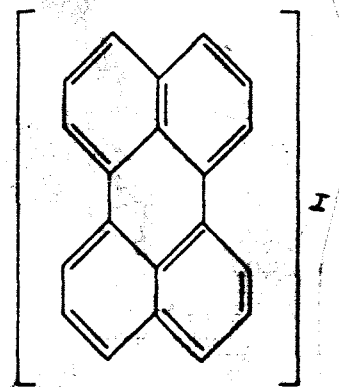
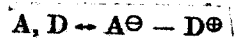


Figure 9. Perylene-iodine complex.

5.4 Additive complexes between two organic molecules. Charge transport complexes

Molecular complexes can also occur through complex formation of two organic substances with acceptor and donor properties. The complexes that are of interest here have quinone, polynitroaromate, tetracyanoethylene, chloranil, bromanil, iodanyl, etc., as acceptor structures, while preponderantly aromatics and their derivatives function as donors. These complexes are only slightly resistant to temperature since their formation proceeds with scant involvement of the components in the structure. They are partially detectable in solution, or even only in solution. Their stability increases with increasing electron affinity of the acceptor and diminishing ionizing energy of the donor. With particularly strong exchange effect there is an electron transfer in the donor-acceptor system. We then speak of charge transfer complexes. Mullikan assumes a complex mesomery of the form



where A, D = state without donor-acceptor activity, and $A^{\ominus} - D^{\oplus}$ = state of transfer of an electron with spin compensation--covalency type bonding state.

The first mesomeric form usually predominates. The second is referred to for clarification of low dipole moments, high conductivity with especially strong exchange effect and paramagnetism. The deepening of color through development of an absorption band in the visible spectrum range is in good agreement with the assumption

$$h\nu = I_D - E_A - W_{AD} \quad (14)$$

where $h\nu$ = energy of the absorption term,
 I_D = ionization energy of the donor,
 E_A = electron affinity of the acceptor,
 W_{AD} = exchange effect energy.

5.5 Heterocyclic compounds

Porphyrine and phthalocyanine are heterocyclic conjugated systems of high coplanarity. In phthalocyanine there are four benzene nuclei bound to the porphyrin base skeleton (fig. 10). Metal-free phthalocyanine and a major part of the metal phthalocyanines are temperature resistant up to 500° C, chemically very stable, subject to sublimation, soluble in sulfuric acid, quinoline and alpha chlornaphthalene. By incorporation of univalent, bivalent, trivalent and tetravalent metals as well as by substitution on the nucleus, variations and perturbations of the conjugation system can be developed. As in all heterocyclics, the number and arrangement of the π electrons is not changed in principle by substitution of a nitrogen atom for a CH group. However the symmetry of the π electron cloud is disturbed by the higher effective nuclear charge of the nitrogen. Furthermore each nitrogen atom carries a single electron pair.

5.6 Natural substances of animal and vegetable origin

Among the natural dyes and vitamins there is a whole series of highly conjugated heterocyclic systems, often with a porphyrin skeleton.

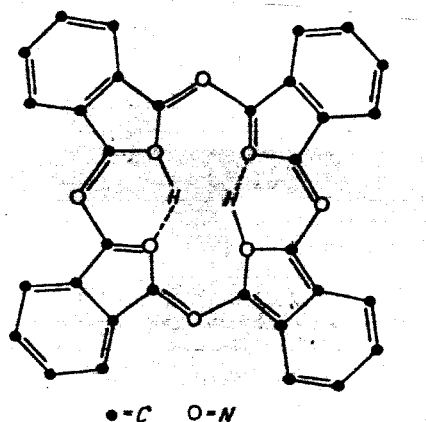


Figure 10. Structure of metal-free phthalocyanine.

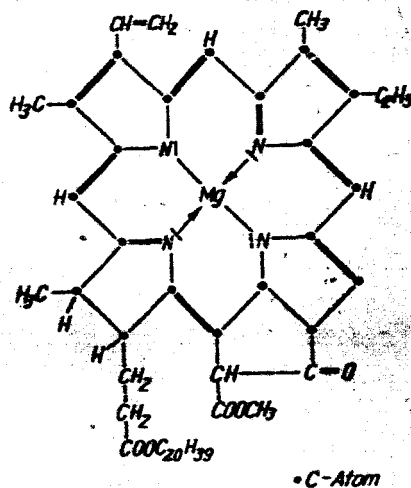


Figure 11. Chlorophyll a.

The plant cell contains chlorophyll (fig. 11) together with carotene and xanthophyll bound to the albumin as a chromoproteid, which is resistant to oxygen and carbon dioxide of the air. Chlorophyll catalytically contributes to photosynthesis.

Ninety-six percent hemoglobin consists of albumin components, and up to four percent is heme. It is the pigment of the erythrocytes. Its physiological function consists in the acceptance and release of oxygen in the blood circulation.

Vitamin B₁₂ is found in raw liver, milk and certain fungi cultures. It crystallizes in dark red needles and contains cobalt in the +3 oxidation stage. Its structural formula shows close relationship to the porphine skeleton.

5.7 Polymers with distinct conjugation system

Normally, organic high polymers are nonconductive. In special cases however, it is possible to create conjugation systems or to extend an existing conjugation system over the entire molecule, by thermal treatment or by the effect of ionizing radiation. Figure 12 shows the conversion of a polyacrylonitrile by thermal treatment in vacuum and in air (ref. 15). Polyvinylene can be formed by splitting off small molecules from saturated macromolecules. It is thus possible to convert polyvinyl alcohols and polyvinyl esters into conjugated systems without occurrence of a break in the carbon chain by the splitting-off of water or alcohols. If the conversion is carried very far, graphite-like structures are produced which may however still contain H-, O- and N-atoms after reaching pyrolysis temperatures of 800° C. In Figure 13 the hypothesized structure of a pyrolysate is shown which is obtained at 700° C from copolymers of divinylbenzene and ethylvinylbenzene (ref. 54).

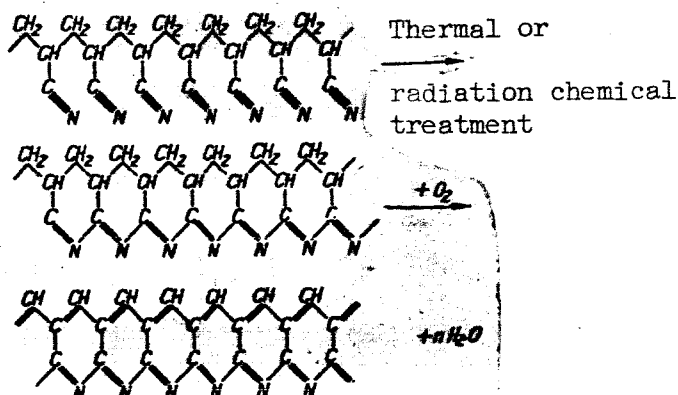


Figure 12. Occurrence of a conjugation system in polyacrylonitrile through thermal or radiochemical treatment (according to Topchiev and Geiderich, ref. 157).

A second way to high conjugated polymers leads over direct synthesis of such compounds by catalysis or by thermal or radiochemical means. This method has been used more and more in recent years. Berlin et al., synthesized polytetracyanoethylene (refs. 55-59a), Marvel et al., polyphthalocyanine (refs. 60 and 61), Krenzel et al., poly Schiff bases (refs. 62 and 63), Wichterle et al., polydicyanoacetylene (refs. 64 and 65), and Pohl et al., polyacene quinone radical polymers (ref. 33). In this work, in addition to other goals, there is the problem of cultivating desired electrical properties by synthesis, through selection of monomeric basic structures and by special methods of polymerization. There should be a field of great activity here in the coming years.

6. Preparation Technique

6.1 Purification methods

Methods can only be selected within the framework of the established 498 physical properties of the individual substances. With the expansion of the conjugation system, the difficulties increase. Organic syntheses produce yields of a magnitude of 50 to 90 percent on the basis of the various reaction possibilities and the complicated ways of synthesis so that the reaction product must initially undergo a coarse purification.

The subsequent purification is indicated by the following:

1. Extraction of foreign materials and unreacted starting products by specific solvents.
2. Repeated recrystallization or precipitation in pure solvents.
3. Fractional distillation or sublimation in high vacuum or in an inert atmosphere.

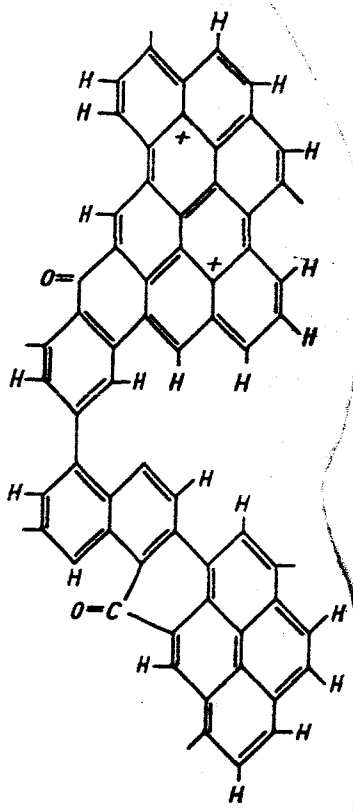


Figure 13. Structure of a pyrolysis product from copolymers of divinylbenzene and ethylvinylbenzene.
+ included radicals (according to Winslow, Baker and Yager, ref. 54).

4. Chromatographic adsorption, division chromatography, gas chromatography, whereby the separating effect of the different migration rates of dissolved or gaseous materials is reduced to a two-phase system.

5. Zone melting, where the separating effect rests on the different solubility of foreign materials in the solid or liquid phase.

6.2 Chemical and physical analysis

The usual criterion for purity of an organic compound is in general a distinct melting point which remains constant upon further purification. As can be seen from the other indications, many semiconducting organic materials do not melt. Aside from the question of purity, the chemical structure /499 and crystal structure must be determined when dealing with compounds synthesized for the first time. No comprehensive survey of the necessary analytic tests can be given in this framework. Only a brief indication of the methods used will be presented.

TABLE 2. PURIFICATION METHODS: ● PREFERRED, ○ APPLICABLE
IN CERTAIN CONDITIONS, ○ NOT APPLICABLE.

Class of materials	Purification method					Bibliography
	1. Extraction	2. Re-crystallization	3. Sublimation	4. Chromatography	5. Zone melting	
5.1 Aromatics	●	●	●	●	●	[40, 67 to 71]
5.2 Organic dyes: triphenyl methane dyes	●	●	●	●	○	[72, 73]
5.3 Halide and alkaline metal complexes	●	●	○	○	○	[74 to 77]
5.4 Additive complexes	●	●	○	○	○	[78 to 80]
5.5 Heterocyclic compounds	●	●	●	●	○	[31, 81 to 84]
5.6 Natural substances	●	●	○	●	○	-
5.7 Polymers	●	●	○	○	○	[33, 60, 61, 85]

1. Elementary analysis furnishes data on the weight fraction of the most important elements for the material and allows inferences concerning impurities.

2. The UV absorption spectra and fluorescence spectra show traces of molecular impurities with a high degree of sensitivity.

3. The infrared spectra characterize bonding relationships in the molecule.

4. Thermal scale measurements and differential thermoanalysis make it possible to follow the course of polymerization and pyrolysis reactions.

5. Paramagnetic electron resonance serves for determination of the density of unpaired electrons in solids.

6. Determination of the molecular weight and its distribution is the most important characterization of high polymer compounds.

In addition to these methods which permit statements on the size and structure of the molecule, there are those methods such as afford determinations on crystalline or part crystalline structure in organic solids, e.g., X-ray small angle scatter, X-ray deflection, and electron microscopy. Also the semiconduction data presented in the following section affords indications on purity and structure of organic substances.

6.3 Crystal growth and doping

Organic molecular crystals are already being used as scintillator crystals. For this purpose methods have been developed for the growth of large anthracene and stilbene crystals (refs. 86-88). Single crystals of polycyclic aromatics can be pulled from the melt (refs. 89 and 90). Zone melted material is allowed to harden slowly by cooling at a fixed temperature gradient. Crystals are obtained with dimensions of several centimeters in each axial direction. By sublimation in nitrogen or under vacuum, single crystals are developed in the form of thin platelets (ref. 91). Growth from the vapor phase is used in preparation of beta phthalocyanine single crystals for example.

Needle-like crystals $30 \times 1.0 \times 0.5 \text{ mm}^3$ are obtained in streaming nitrogen at 10 to 50 Torr (refs. 31, 91 and 92). Detailed data on seed formation, growth conditions and absorption properties of growing crystal surfaces are presented

by Honigmann (ref. 93) in the growth of $10 \times 10 \times 3 \text{ mm}^3$ hexamethylene tetramine single crystals. Complexes can be obtained in single crystal form with dimensions of several millimeters by cooling their solutions (ca. $10^\circ/\text{week}$). The crystallization processes in polymers proceed principally as in lower molecular organic compounds. Polyethylene, polyoxymethylene, poly-tri-methyl pentene have recently been obtained as single crystals (ref. 86). Polymers with distinct conjugation systems have been prepared so far only with crystalline partial domains.

The doping of organic compounds with organic and inorganic additions has been undertaken using single crystals and polycrystalline as well as amorphous materials.

Northrop and Simpson (ref. 53) were able to obtain only a very 500 scanty content of impurities by melting polycrystalline aromatics. Simultaneous vaporization, because of very different vapor pressures that often arise, leads to no better results. For this reason the authors used the method of vaporization of portions of an intimate mixture of both components. Polymers were doped with inorganic additions by swelling in aqueous salt solutions and subsequent drying (ref. 15). Epstein and Wildi (ref. 35) doped poly copper phthalocyanine by a nonstoichiometric incorporation of copper atoms. Special polymerization catalysts can also take over the function of a dopant (ref. 95). In complexes the excess of donor or acceptor substances has a doping effect (ref. 20). Substances with strong acceptor or donor effect are sprayed in the form of solutions onto polycrystalline powder or thin layers for doping of aromatics or heterocyclic compounds. After evaporation of the solvent there is a complex formation on the surface of the microcrystal (refs. 96 and 97).

7. Measurement Methods

Known methods of measurement are generally used for investigation of the electrical properties of organic compounds. In order to include substances with high specific resistivities, the method must be designed partly with a relinquishing of extreme accuracy of measurement to the limit of their sensitivity.

7.1 Contacting method

Organic semiconductors exist for the most part as polycrystalline or amorphous powder in the form of vapor-deposition layers or as single crystals with scant mechanical stability. A number of methods are utilized for contacting.

7.1.1 Contacting with set-on metal electrodes

Flat metal electrodes (noble metals, copper, brass) are set (ref. 35) on semiconductor blanks prepressed at a few thousand kp/cm^2 . A pronounced lowering of the contact resistance is obtained (ref. 2) by use of a pressure of 200 to 300 kp/cm^2 on the contact surfaces. The use of methods applying single crystals with gold-plated brass tips (ref. 38) or platinum wires (ref. 98) as electrodes requires much experimental dexterity.

7.1.2 Contacting with metal layers

Metal layers can be prepared by fusing on metal foils, by vapor deposition, or by the pressing on of metal powder. Riehl (refs. 51 and 52) melts platinum foils on naphthalene single crystals and finds Ohm's law supported up to $10^3 \text{V}/\text{cm}$. Mette and Pick contact anthracene in this way but find poor semiconductivity above 100°C , with improvement through tempering (ref. 67).

Eley presses platinum foil with 80 kp/cm^2 onto the semiconductor (ref. 99). Bradley uses nickel foils for measurements of conductivity under maximum pressures (ref. 100). Vapor-deposited metal layers are especially suited as light-permeable electrodes. They have no polarization separation in high ohmic material (ref. 69). The use of vapor deposited lead leads to very well-adhering layers (ref. 53). Pressed-on metal powder layers (Ag, Cu, Al) of a few tenths of a millimeter thickness yield mechanically stable contacts with good electrical properties (ref. 101). They are particularly suitable where a high heat transfer to the semiconductor is required (ref. 84).

7.1.3 Contacting with mercury, pastes, suspensions and electrolytes

Mercury effects a contact in a mechanically and thermally protective manner (ref. 67). The contacts are detachable. Graphite suspensions or silver paste for which a fine grain is a stringent requirement are applied to the surfaces of the semiconductors and dried (refs. 37 and 102). This method makes spot contacts possible. It is useful particularly for single crystals of small and minimum dimensions. Kallman and Pope use electrolyte electrodes (NaCl-, NaI-solutions) for injection of charge carriers in anthracene (refs. 103 and 104).

7.2 Measurement of conductivity

As shown in figure 1 the materials used as organic semiconductors go beyond many orders of magnitude of specific resistance. It often appears to be specially advantageous to include in the study the high ohmic starting substances which have a semiconducting structure only as a result of special treatment. In the second place the range of temperature measurement should be extended as far as possible toward low temperatures. These requirements

entail measuring equipment for resistance measurements to ca. $10^{16} \Omega$. By spe-

cial choice of sample geometry, specific resistance to $10^{18} \Omega \text{ cm}$ can be included. A typical measuring cell is shown in figure 14. Such cells are made of glass and quartz or of metal. The electric lead-ins are fused in with creepage path extensions, or with metal cells insulated from each other by Teflon or polystyrene. A heating system with resistance heating or thermostats with liquid circulation furnish a slowly rising or falling temperature with a homogeneous temperature distribution in the region of the sample.

- | | |
|----------------------|-----------------------|
| 1. Vacuum connection | 5. Compression spring |
| 2. Thermo-element | 6. Adjusting screw |
| 3. Heating coil | 7. Sample |
| 4. Copper electrode | 8. Gas Inlet |
- (According to Sehr, Labes et al., ref. 78)

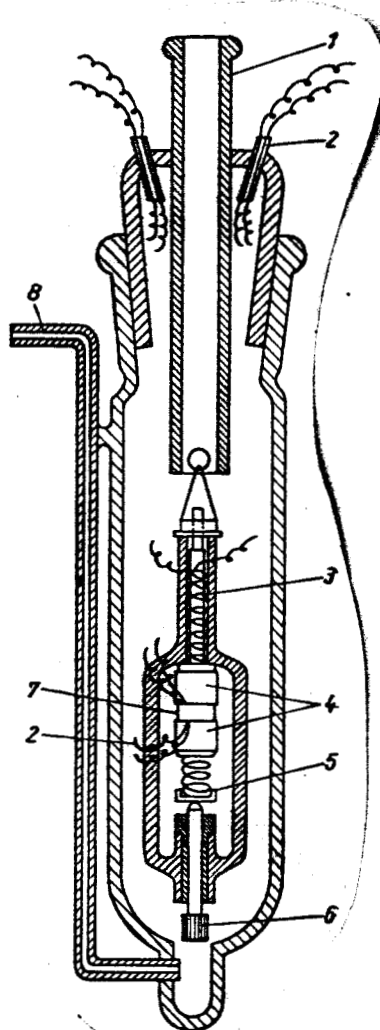


Figure 14. Measuring cell for conductivity and thermal voltage measurements.

The elevation of temperature must not exceed $1^{\circ}\text{C}/\text{min}$ because of the /502
slight heat conductivity of organic substances. Thermoelements or resistance
thermometers are advantageously placed in the immediate vicinity of the sam-
ple or in a boring in the sample (ref. 105). Conductivity measuring cells
must allow selective use of high vacuum and streaming inert gases. Special
construction makes it possible to introduce aggressive gases or to make mea-
surements under gas pressures up to $12\text{ kp}/\text{cm}^2$ (ref. 106). Measuring samples
with resistances of up to $10^8\ \Omega$ are easily handled with Wheatstone bridges and
compensating circuits. With very high ohmic value samples only electrometer
tube amplifiers and oscillator capacitor electrometers meet the requirements.
A meticulous electrostatic shielding of measuring cells and leads is an abso-
lute necessity.

7.3 The measurement of thermal voltage

In recent years the study of differential thermal voltage has been in-
creasingly emphasized for explanation of charge transport in organic semi-
conductors (refs. 18, 29-34, 38, 54, 57, 58, 78, 80, 84, 101, 107-117). Con-
ditioned by high ohmic measuring samples, methods were worked out to allow
measurements of thermal voltage for sample resistivities up to $10^{12}\ \Omega$.

Labes, Sehr and Bose (refs. 78 and 80) use the apparatus of figure 14.
The sample is placed under spring pressure between two copper electrodes, one
of which can be supplementarily heated. The temperature gradient is deter-
mined by means of thermoelements. Hamann and Starke (ref. 84) measure thermal
voltage of high ohmic samples under high vacuum between two copper electrodes
that are mutually insulated by Teflon sleeves. The temperature gradient is
adjusted by two silicon oil thermostats. Its measurement is accomplished by
platinum resistance thermometers. An oscillator capacitor electrometer with
an input resistance of $\geq 10^{15}\ \Omega$ and a full scale reading of 1 mV serves as a
sensitive indicating apparatus. The indication of stationary relationships is
provided by a writing recorder.

Cardew and Eley (ref. 108) use a device similar to that shown in figure
14, except that in addition to a heating coil for adjusting an average tem-
perature, two supplementary heaters are available for the two electrodes so
that the temperature gradient as in (ref. 84) can be reversed during the mea-
surement. If samples of 10^{11} to $10^{12}\ \Omega$ are measured, asymmetrical time-
constant voltages of about 200 mV occur in the samples which must be com-
pensated (cf. ref. 84). Wildi measures pyrolyzed polymers between gold-plated
electrodes, one of which is held at 23°C while the other is radiation-heated
to 100°C (ref. 110). During the measurement, heat conduction can cause heat-
ing of the unstabilized electrodes. Slough (ref. 107) using an arrangement
with two platinum-coated copper electrodes at resistances of $10^{10}\ \Omega$ and tem-
perature gradient 0, finds contact potentials from 0 to 20 mV. Measurements

of the Seebeck coefficients are carried out at temperature gradients of 20° C (difference between 120° and 140° C).

Nelson and Schroeder (refs. 32 and 115) measure the thermal voltage qualitatively (determination of the sign) on thin dye films. An electrode is heated in a high ohmic apparatus by a strip lamp. Asymmetrical voltages can be substantially reduced by careful and clean preparation of the sample.

Fielding and Gutman (ref. 31) measure single crystals of copper /503 phthalocyanine along the needle axis. Their apparatus consists of a bored Teflon block in which the single crystal is fixed by silver paste to two silver wire windings 2 mm in diameter. The temperature gradient is set in the range from 70° to 130° C by a carefully shielded resistance heating apparatus. The thermoelements are removed during the measurement. For capacitance toward

ground a value of 8 pf is indicated, which corresponds at $10^{12} \Omega$ sample resistance to a time constant of ≤ 50 sec.

7.4 Measurement of the Hall effect

In order to avoid experimental difficulties that occur in measurement of the Hall effect through drift and noise, measurements were first undertaken on low ohmic organic complexes and conductive polymers. Complex compounds uniformly show no measurable Hall effect, which permits a limiting of their Hall

mobility μ_H toward the top: $\mu_H \leq 0.01$ to $0.04 \text{ cm}^2/\text{Vsec}$ (refs. 22, 29 and 101).

Hall voltages are found in poly copper phthalocyanine (refs. 35 and 36) and polymer-metal mixtures (ref. 117). Balabanov and Frankevich (ref. 120) could not confirm measurements on polymeric copper phthalocyanine. Epstein and Wildi (ref. 35) use the measuring apparatus in figure 15 for pressed samples of $0.9 \times 0.3 \times 0.8 \text{ cm}^3$, contacted with silver paste, vapor-deposited silver, or pressed-on metal contacts. All contacts yield reproducible results. Measurements can be made at temperatures above room temperature in vacuum or selected gas atmospheres. Hall mobility was measured for the first time in organic molecular crystals in 1962 by Heilmeyer, Warfield and Harrison (ref. 37) using an oscillator capacitor electrometer (fig. 16a) for measurement of the current passing through the sample as well as for detection of the Hall voltage. To separate measured value and noise, the electrometer output voltage had to be written and planimetered as a function of time. Figure 16b shows the curve thus obtained as a function of the magnetic field for single crystals of metal-free phthalocyanine. Delacote and Schott determined the Hall voltage of copper phthalocyanine single crystals at 400° to 650° K in air (ref. 38).

In a subsequent work Heilmeyer and Harrison (ref. 39) used a tech- /504 nique of differential measurement. A copper phthalocyanine single crystal

($20 \times 3 \times 0.2 \text{ mm}^3$) is fixed to a quartz sample holder. The sample holder is heated by resistance heating, with a pause of 3 hours after each change of temperature, to ensure complete temperature equilibrium in the sample and to

1. Insulation
2. Sample
3. Noninductive heating coil
4. Magnet
5. Water cooling
6. Gas outlet
7. Vacuum connection
8. Gas inlet
9. Aerating valve

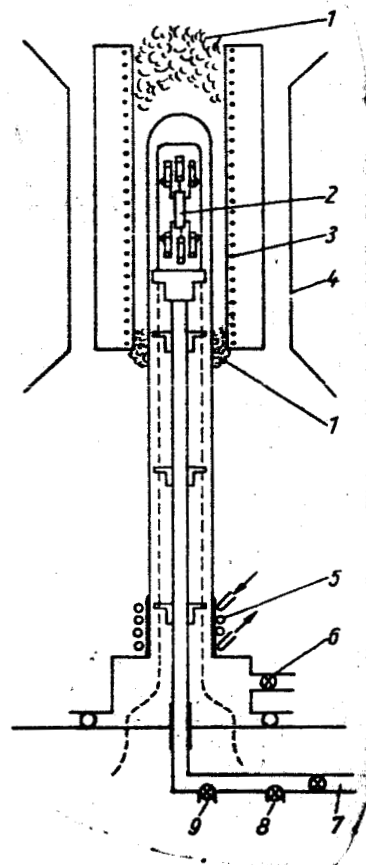


Figure 15. Measurement cell for Hall effect measurements (according to Epstein and Wildi, ref. 35).

avoid drift. The Hall voltage is delivered by a shielded cable to the grid of two electrometer tubes (fig. 17). With this circuit, drift and noise, which are capacitively coupled, are well compensated at the output. The high stability must be achieved at the cost of reduced sensitivity. Half of the applied voltage appears over the grids of the input tubes, so that for the minimum measurable mobility

$$\mu_{Hmin} = V_{Hmin} \frac{l}{w} \frac{1}{B_{max} V_{Amax}} ;$$

where V_{Hmin} = minimum detectable Hall voltage = 0.15 mV,

l/w = length/thickness of the crystal = 7.5,

B_{max} = maximum magnetic induction = 6.5 kG, and

V_{Amax} = maximum applicable voltage = 2 V.

$$\mu_{Hmin} = 9 \text{ cm}^2/\text{Vs} .$$

/505

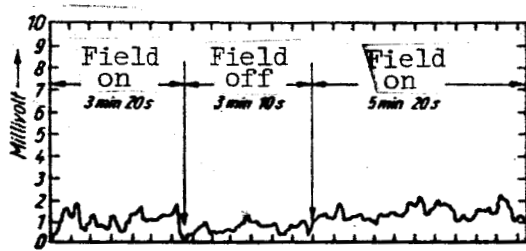
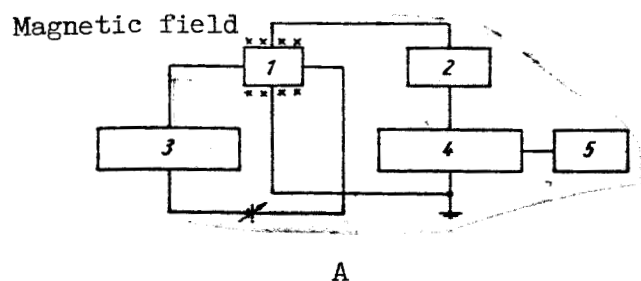


Figure 16a. Block circuit diagram of a Hall effect measuring apparatus, (ref. 37).
1, Sample; 2, Compensating stage; 3 and 4, Oscillator capacitor electrometer; 5, Recording device.

Figure 16b. Voltage characteristic as function of time on Hall probes, (ref. 37).

All insulations are made with selected Teflon pieces with a resistivity of

$\geq 5 \cdot 10^{15} \Omega$ at 400°K . If this value is exceeded, mobilities of $\geq 100 \text{ cm}^2/\text{Vsec}$ can be simulated by surface leakage currents. Gobrecht et al., (refs. 118 and 119) also present Hall effect measuring apparatus and electrode devices for high ohmic material.

7.5 Photoelectric measuring processes

Organic compounds are tested in the form of single crystals, and as vapor-deposited and separated layers for their photoelectric properties. For measurement of surface photoconduction, the methods of transverse field illumination are used for measurement of volume conductivity of longitudinal field illumination (ref. 121). The necessary light-permeable cover electrode in

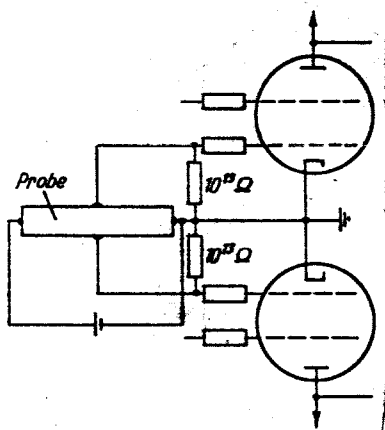


Figure 17. Schematic for Hall effect apparatus with two electrometer tubes (according to Heilmeyer and Harrison, ref. 39).

longitudinal field illumination is advantageously made as a network of finely-dispersed metal particles and metal oxides, for the prevention of barrier layers (ref. 122). A typical metal cell is shown in figure 18. Cells of this kind consist of: a) a glass or metallic jacket with vacuum connection; b) an adjustable sample holder; c) a window of glass or quartz for light inlet; d) highly insulated leads; and e) a tempering device.

For development of continuous or intermittent light of desired spectral composition, there are: f) devices for modulation of light intensity; and g) monochromators or filters arranged in the beam path.

For short time measurements Boroffka (ref. 69) used a 40 cm /506
diameter disk from which a 15 mm wide strip had been cut from a quarter of the periphery. The rotation rate was 4800 rpm. Ahead of the sector disk there was a camera connection, with opening time equal to the pulse duration. The

transition interval of the light impulses thus produced was $2 \cdot 10^{-5}$ sec. Kepler (ref. 40) produces light pulses of 2 μ sec duration with a xenon flash lamp. Polarized light flashes with slight intensity but with a high serial

1. Light source
2. Quartz window
3. Vacuum connection
4. Shield
5. Electrometer connection
6. Smoothed connection
7. Battery connection
8. Thermoelement
9. Sample
10. Teflon disk
11. Copper block
12. Glass support

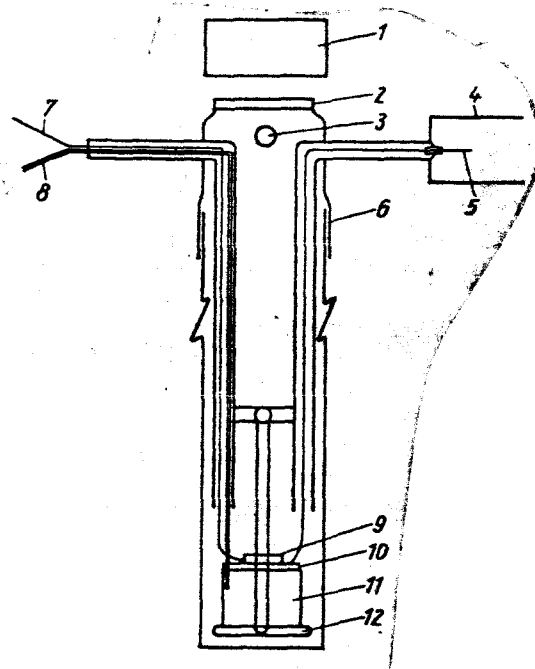


Figure 18. Measuring cell for photoconduction measurements (according to Kommandeur, Korinek and Schneider, ref. 94).

frequency of 10^8 to 10^9 cycles can be produced by using Kerr cells between two polarizers (ref. 123).

Light intensity is controlled over a wide range through the following measures: a) filter or metal grid in the beam path; b) variation of illumination intensity of the light source; and c) change of the magnitude of the inlet slit (refs. 98, 124 and 125). It is necessary for the determination of the quantum efficiency (number of charge carriers/number of absorbed photons) to make absolute measurements of the light intensity in the spectral range in question.

Sano (ref. 70) uses vacuum thermoelements with a sensitivity of $5.6 \mu\text{V}/\mu\text{W}$ and a time constant of $3.3 \cdot 10^{-2}$ sec for low light intensity. At maximum intensities of $6 \cdot 10^{18}$ photons/ cm^2 sec, PbS photoelements or germanium transistors can be introduced. Putseiko measures the energy distribution of the air behind the monochromator gap with a thermocolumn and galvanometer (ref. 126).

In addition to investigations of photoconduction in continuous and intermittent light in dependence upon temperature and wavelength of the absorbed light, methods are used which serve for determination of the sign of the photo-induced charge carrier and its mobility.

Akimov (ref. 127) developed a form of dynamic capacitor proposed by Witol (ref. 128) for measurement of the contact potential and the sign of the charge carrier. The dark electrode consists of a cylindrical glass finger vapor-coated with platinum which is divided into four sectors by four narrow cuts 1 mm wide. Three sectors are vapor-coated with organic substance and one remains free for purposes of comparison. An oscillating electrode is brought

opposite the coatings at a distance of 1.0 to 1.5 mm. This arrangement uses the principle of the oscillator capacitor whereby the dielectric is formed by the semiconducting substance.

Putseiko (ref. 126) uses the capacitor method of Bergmann (ref. 129) for determination of the charge carrier sign. A thin pressed layer of the substance to be tested is placed between two insulating light-permeable plates. This construction is in a capacitor. If it is now illuminated with intermittent light, an alternating voltage occurs in this device. By application of an additional voltage, the sign of the photoinduced carrier can be determined.

Kepler can determine the mobility of the photoinduced carrier in anthracene with a similar apparatus (ref. 40) figure 19 shows the block diagram of his arrangement. Near the illuminated surface a cloud of charge carriers develops. Its movement through the crystal in the electric field is observed on the oscilloscope. The pulses have a duration t of a few hundred μsec . If space charge effects and surface currents are to be prevented, $t \sim 1/V$ (V =applied voltage) and $t \sim d$ (d =crystal density). The mobility for electrons and holes (the measurement is possible simply through reversal of the applied voltage) follows the equation

$$\mu = d^2/Vt. \quad (15)$$

8. Measurement Results

The constantly increasing experimental material makes it possible in spite of the much scattered measurement values of the different authors to draw a series of interesting conclusions.

8.1 The nature of the charge carrier

In the materials classes discussed under section 5, conduction processes are determinative on the basis of electrons and holes. Proton conduction in certain polymers and natural substances with hydrogen cross linkages, and proton conduction in ice are only indicated here (ref. 131). The relatively

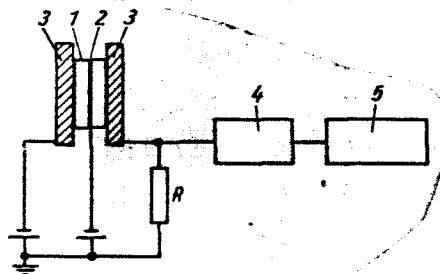


Figure 19. Capacitor-method measuring device. 1, Sample; 2, ring electrode made of silver paste; 3, glass electrode; 4, amplifier; and 5, oscilloscope.

high conductivity of complexes and polymers with an expanded conjugation system (Table 3) supports the above finding. Also with an assumption of maximum ion concentration, conductivities of this kind in the organic solid are impossible. In addition, there is the fact that with use of high current densities over months-long periods of time, there is no detectable reduction of conductivity (refs. 51 and 166). The successful Hall experiments with polymeric and monomeric phthalocyanines (refs. 35-39) also are evidence against ionic conduction.

From the lack of a measurable Hall effect it can be concluded that there is very slight mobility of the charge carrier, and that conduction mechanisms are conceivable that exclude a deflection of the moved charge carriers in the applied magnetic field (see section 4.4, The hopping process). In long chain polymers, particularly in the case of pyrolyzed polyacrylonitrile, the mobility

of charge carriers could be determined as $\mu_H \leq 0.003 \text{ cm}^2/\text{Vsec}$. If transfers of charge carriers are possible only from chain end to chain end, the path of the charge carrier is substantially predetermined by the statistically tangled chain molecules (ref. 4, page 300). Also the correlation of the thermal excitation energy of the charge carrier and the long wavelength limit of photoconductivity as found for complexes and dyes indicates the electronic character of charge transport (refs. 132-134) (Table 4).

8.2 The excitation energy of the charge carrier

Organic semiconductors in the temperature dependency of their electric conductivity in broad temperature ranges are governed by equation (6). Figure 20 shows this behavior for a single crystal of metal-free phthalocyanine (ref. 31). The excitation energy of charge carrier E which is thus determined is a function of the π electron count in polycyclic aromatics (cf. fig. 5) and is in good agreement with the long wavelength absorption edge and the minimum optical excitation energy for photoconduction. The same is true of ionic dyes and certain complexes of two organic molecules (table 4). These interrelationships show the significance of the short range order, i.e., the structure of the individual molecule, for semiconductor properties in the classes of materials in question. The potential barriers between the individual molecules are overcome by the tunnel effect, or the excitation levels of the individual molecules are united by weak exchange forces of van der Waals type to form bands.

The behavior of complexes with conductivities $\sigma > 10^{-3} (\Omega \text{ cm})^{-1}$ and excitation energies of the magnitude 0.02 eV is interpreted by Airapetjanc and Rozenshtein by the presence of an occupied band of the metallic type, formed by donor and acceptor levels (ref. 116). Here the optical excitation energy exceeds the thermal excitation energy several times over.

In general polymers have thermal excitation energies that exceed the optical excitation energies. Only by thermal treatment or precision synthesis of extended conjugation systems are their thermal excitation energies of the magnitude of 0.2 eV. This behavior can be clarified by assumption of a

TABLE 3. VALUES OF DIFFERENTIAL THERMAL VOLTAGE

Material	σ 20° C (Ω cm) ⁻¹	E* (eV)	α (μ V/degree)	Reference
Complexes				
3-chloranil-5-paraphenylene diamine	10 ⁻⁷	1.32	+1000	[101]
3-chloranil-5-paraphenylene diamine	10 ⁻⁷	1.14	+1100	[30]
Chloranil diaminodurel	10 ⁻⁴	0.58	+ 300	[101]
Chloranil diaminodurel	1.4 · 10 ⁻⁵	-	+ 300	[78]
2 · TCNQ-trimethylammonium	4	0.28	- 100	[29]
Naphthacene-1.8 · Na	4.8 · 10 ⁻⁸	0.64	neg.	}
1,2-benzanthracene-Na	1.1 · 10 ⁻¹⁰	1.32	neg.	
2,3-benzacridine-Na	1.9 · 10 ⁻⁹	1.74	neg.	
Naphthacene-1.76 · I ₂	10 ⁻¹⁰	1.1	pos.	
1,2-benzanthracene-1.74 · I ₂	10 ⁻¹²	1.8	pos.	}
2,3-Benzacridine-2 · I ₂	9.5 · 10 ⁻¹⁰	2.4	+ 350	
2 · TCNQ-triethylammonium	≤ 4	0.28	- 100	[29]
TCA-polyvinyl naphthalin (= PVN)	10 ⁻¹⁰ at	1.20	+2700	}
TCA-(PVN) ₂	10 ⁻⁸ T =	1.10	+2300	
TCA-PVN (isotactic)	10 ⁻¹² 406	1.24	+2400	}
Chloranil-PVN	10 ⁻¹⁰ OK	1.16	+1400	
3,8-diaminopyrene-chloranil	10 ⁻³	0.30	+ 5	}
3,10-diaminopyrene-chloranil	10 ⁻⁵	0.80	+ 400	
3,8-diaminopyrene-bromanil	10 ⁻³	0.30	+ 100	
3,8-diaminopyrene-iodanil	10 ⁻⁶	0.82	+ 700	
Perylene-I ₂	0.3...0.5	0.02...0.04	- 10	}
Coronene-I ₂	10 ⁻⁸	1.0	+1500	

* Calculated with $\sigma = \sigma_0 \cdot \exp (- E/2 k T)$

TABLE 3. CONTINUED

Material	σ 20° C (Ω cm) ⁻¹	E* (eV)	α (μ V/degree)	Reference
Organic dyes with ion bonding				
Crystal violet	-	-	neg. (vacuum) positive (air)	[115]
Crystal violet	10-11	1.78	neg.	[116]
Crystal violet	-	-	-300	[32]
Capri blue	10-13	1.67	neg.	[116]
Malachite green	-	-	neg. (vacuum) positive (air)	}
Ethyl violet	-	-	neg. (vacuum) positive (air)	
Methyl green	-	-	neg. (vacuum)	
Brilliant green	-	-	neg. (vacuum) positive (air)	
Pinacyanene	-	-	neg. (vacuum) positive (air)	}
Pinacyanene	10-12	1.9	neg.	
Rhodamine B	-	-	neg. (vacuum) positive (air)	}
Auramine	-	-	neg. (vacuum) positive (air)	
Erythrosine	-	-	pos. (vacuum) positive (air)	
Eosin	-	-	pos. (air)	}
Eosin	10-14	2.3	pos.	
Acridine orange	-	-	pos. (air)	}
Bengal rose	-	-	pos. (air)	
Congo red	-	-	pos. (air)	
Cryptocyanine	-	-	pos. (air)	
3,3-diethyl thiocarbocyanine	-	-	pos. (vacuum)	[115]

*Calculated with $\sigma = \sigma_0 \cdot \exp(-E/2 k T)$

TABLE 3. CONTINUED

Heterocyclic compounds

Material	$\sigma_{200} \text{ C } (\Omega \text{ cm})^{-1}$	$E^* \text{ (eV)}$	$\alpha \text{ } (\mu\text{V/degree})$	Reference
Cu-phthalocyanine (Pc)	10^{-13}	1.7		[116]
Metal free Pc, α	$(1.28 \pm 0.13) \cdot 10^{-10}$	1.42 ± 0.08	pos. + 1250 ± 60	
Metal free Pc, β	$(2.38 \pm 0.25) \cdot 10^{-15}$	1.74 ± 0.08	+ 670 ± 40	
α -CuCl-Pc	$(1.0 \pm 0.10) \cdot 10^{-7}$	0.60 ± 0.04	+ 910 ± 50	
β -CuCl-Pc	$(5.0 \pm 0.50) \cdot 10^{-14}$	1.56 ± 0.08	+ 1170 ± 60	[34]
α -Ni-Pc	$(7.1 \pm 0.10) \cdot 10^{-9}$	1.20 ± 0.06	+ 970 ± 50	
β -Ni-Pc	$(2.5 \pm 0.25) \cdot 10^{-15}$	2.28 ± 0.12	+ 1280 ± 70	
α -Zn-Pc	$(2.13 \pm 0.20) \cdot 10^{-8}$	0.86 ± 0.04	+ 960 ± 50	
β -Zn-Pc	$(2.5 \pm 0.25) \cdot 10^{-12}$	1.44 ± 0.08	+ 1750 ± 90	
β -Cl-InCl-Pc	$(2.6 \pm 0.25) \cdot 10^{-14}$	1.64 ± 0.08	- 1610 ± 80	
Metal free Pc: α	$1.0 \cdot 10^{-10}$	1.54 ± 0.08	+ 1130 ± 55	
α	$5.0 \cdot 10^{-12}$	1.36 ± 0.06	+ 1060 ± 50	
α (β)	$2.5 \cdot 10^{-12}$	1.46 ± 0.08	sublimated + 1620 ± 80	
α, β	$5.0 \cdot 10^{-14}$	1.16 ± 0.06	(α (β) tempered at 2500°C) - 70 ± 4	[84]
β	$9.1 \cdot 10^{-17}$	1.94 ± 0.10	+ 70 ± 4	
β, γ	$3.8 \cdot 10^{-14}$	1.66 ± 0.08	+ 1400 ± 70	
β, α	$7.1 \cdot 10^{-15}$	1.94 ± 0.10	(β ground) + 910 ± 50	
β, α	-	-	- 1310 ± 70	
γ, β	$1.04 \cdot 10^{-10}$	1.46 ± 0.08	(β, α) tempered in vacuum + 910 ± 50	
γ, α	$7.7 \cdot 10^{-11}$	1.42 ± 0.08	+ 1075 ± 60	
Cu-Pc	-	-	+ 700	[38]
β -Cu-Pc (single crystal)	-	1.64 ± 0.03	+ 50	[31]

*Calculated with $\sigma = \sigma_0 \cdot \exp(-E/2 k T)$

TABLE 3. CONTINUED

Polymers

Material	Temperature	σ_{200}^C ($\Omega \text{ cm}$) ⁻¹	E* (eV)	α ($\mu\text{V}/\text{degree}$)	Reference
Polyacrylonitrile	580° C Pyrolysis temperature in air	$1.4 \cdot 10^{-4}$	0.75	pos.	[116]
	640° C Pyrolysis temperature in air	$7.0 \cdot 10^{-3}$	0.52	+ 88	
	700° C Pyrolysis temperature in air	0.17	0.37	+ 45	
	580° C Pyrolysis temperature in vacuum	$5.9 \cdot 10^{-3}$	0.44	- 42	
	640° C Pyrolysis temperature in vacuum	$9.0 \cdot 10^{-2}$	0.32	- 17	
	700° C Pyrolysis temperature in vacuum	0.9	0.20	- 2	
		Before heating in vacuum		Before heating in vacuum	
Polyacrylonitrile	520° C	2.2 · 10 ⁻⁴	-	- 104	[114]
	580° C	2.2 · 10 ⁻⁴	-	- 42	
	600° C	3.5 · 10 ⁻³	-	- 48	
	620° C	3.0 · 10 ⁻³	-	- 22	
	640° C	2.5 · 10 ⁻²	-	- 17	
	640° C	5.6 · 10 ⁻²	-	- 15	
	640° C	5.9 · 10 ⁻²	-	+ 88	
	670° C	0.24	-	+ 61	
	680° C	0.67	-	- 8.8	
	700° C	0.56	-	+ 54	
	700° C	0.72	-	+ 45	
	710° C	2.1	-	- 2	
*Calculated with $\sigma = \sigma_0 \cdot \exp(-E/2kT)$		2.7	-	+ 36	0.4

TABLE 3. CONTINUED

Polymers Continued

Material	$\sigma_{200}^{\circ} \text{C} (\Omega \text{ cm})^{-1}$	E* (eV)	α ($\mu\text{V}/\text{degree}$)	Refer- ence
7300 C Pyrolysis temperature in vacuum	Before heating in vacuum 2.4		Before heating in vac. + 26 + 0.7	[114] [117]
Various polymers and iron powder				
Polyacrylonitrile	4000 C NH_3 doped 5000 C NH_3 doped	-	+ 5 + 75	
(Pyrolysis temperature)	5000 C CuCl_2 doped	-	+ 108	[18]
	5000 C not doped	-	+ 72	
	5000 C (NH_3) doped	-	+ 110 + 81	
Values of differential thermal voltage polymers				
Polyacene quinone radical polymers (PAQR) reacted with dibenzopyrene at 3060 C				
Pyrene at 3060 C	1.1 · 10 ⁻³	0.412	- 19	
Pyrene at 2530 C	1.3 · 10 ⁻⁴	0.310	+ 69.6	
Penanthrene at 2530 C	6.3 · 10 ⁻⁵	0.396	+ 21.8	[33]
Chrysene at 2530 C	1.0 · 10 ⁻⁵	0.410	+ 155.9	
Anthracene at 2530 C	6.3 · 10 ⁻⁶	-	+ 122.5	
Polyvinyl naphthalene complex with Tetracyanoethylene	1.2 · 10 ⁻⁶	0.514	+ 345.5	
1/2 · Tetracyanoethylene	3.2 · 10 ⁻¹⁵	1.20	+ 2700	
Tetracyanoethylene (isotactic)	7.4 · 10 ⁻¹⁵	1.10	+ 2300	[107]
Chloranil	2.8 · 10 ⁻¹⁵	1.16	+ 2400	
Reaction product	7.2 · 10 ⁻¹⁵	1.24	+ 1400	
Pyromellitnitrile - H_2S	(130...17000 Ω)	-	- 50	[110]
	22.0	0.03	+ 6	
	7.1	0.04	+ 9	
TCA-Chelate + Iron powder various composition	0.135	0.04	+ 9	[58]
	3.4 · 10 ⁻⁴	0.10	pos.	
Glycine	-	-	- 360(1530C)	[108]
*Calculated with $\sigma = \sigma_0 \cdot \exp (-E/2 k T)$	-	-	- 730(1660C)	

TABLE 4a. COMPARISON OF THERMAL AND OPTICAL EXCITATION ENERGIES
(ACCORDING TO INOKUCHI AND AKAMATU, REF. 2)

Material	Thermal excitation energy (eV)	Optical absorption edge (eV)	Excitation energy for photoconduction (eV)
Perylene	2.0	2.5	2.3
Coronene	1.7	1.9	-
Indanthrazine	0.66	0.65 to 0.7	0.80
Indanthrone	0.63	0.65	0.74
Flavanthrone	0.70	0.7 to 0.75	0.76
Pyranthrone	1.07	0.75 to 0.8	0.85
Pyranthrone	1.06	0.8 to 0.85	1.14
Ovalene	1.13	1.2	1.20
Violanthrone	0.85	0.8	0.88
Violanthrone	0.78	0.75	0.84
Isoviolanthrone	0.82	-	0.85
Isoviolanthrone	0.75	0.7 to 0.75	0.93

TABLE 4b. COMPARISON OF THERMAL AND OPTICAL EXCITATION ENERGIES
(ACCORDING TO VARTANYAN, REF. 176)

Material	Thermal excitation energy		Position of long wavelength absorption edge (nm)
	(eV)	(nm)	
Malachite green	1.67	740	655 to 750
Fuchsin	1.79	690	580 to 700
Crystal violet	1.78	694	630 to 710
Uranine	2.05	603	510 to 605
Eosin	2.30	536	520 to 590
Erythrosine	2.22	566	530 to 600
Phloxine	2.07	597	530 to 600
Rhodamine B	2.10	588	578 to 630
Fluorescein	2.44	506	490 to 530
Trypaflavin	2.3	536	480 to 540
Capri blue	1.67	740	700 to 780
Thionine	1.83	675	650 to 700
Indigo	1.75	705	660 to 720
Pinacyanene	1.90	650	642 to 720
Metal free phthalocyanine	1.7	725	688 to 790
Copper phthalocyanine	1.7	725	685 to 780
Zinc phthalocyanine	1.7	725	714 to 810

temperature-dependent mobility, but it is only validly explained by Hall effect measurements. Epstein and Wildi (ref. 35) find a temperature independent carrier concentration in one case for a poly copper phthalocyanine pyrolyzed at 450° C. The measured excitation energy is then identical with the potential

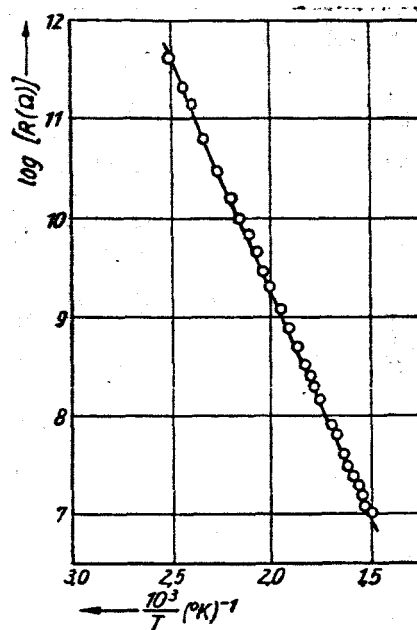


Figure 20. The temperature dependency of direct current resistivity of metal-free phthalocyanine. Measurement on a single crystal \perp to the b axis \parallel (010) \perp (001) (according to Fielding and Gutman, ref. 31).

barriers between the molecules, which are overcome in charge transport by hopping processes.

8.3 Concentration and mobility of the charge carrier

In the simplest case, Many, Harnik and Gerlich (ref. 135) proceed from the fact that the effective carrier concentration must maximally equal the number of π electrons. In polycyclic aromatics

$$N_{\max} \approx 10^{23} \text{ cm}^{-3}.$$

The actual value N_0 is written as $N_0 = \alpha N_{\max}$, $\alpha \ll 1$. Since there are 514 weak bonding forces in molecular crystals, $N_{\min} \approx 10^{20} \text{ cm}^{-3}$ can be represented. The available measuring values (refs. 67, 106, and 136-138) are according to

$$\sigma = e \mu n,$$

$$\sigma = e \mu N_0 \exp(-E/kT)$$

For the product μN_0

$$10^9 \leq \mu N_0 \leq 10^{22}, \quad 10^{20} \leq N_0 \leq 10^{23}.$$

Its variations over 23 orders of magnitude must be conditioned by various mobilities. Table 5 shows the values calculated by Many et al. (ref. 135) for the carrier mobility, which stand in a certain relationship to those of thermal excitation energy. This correlation is evidence of a tunnel process of the charge carrier from molecule to molecule.

The measurements presented in table 3 for the differential thermal voltage are drawn into calculation of mobility of electrons and holes. If there are no further measurements it is an open question whether there is intrinsic or extrinsic conduction.

In the area of intrinsic conduction, with application of the bands model for isotropic nondegenerate semiconductors, and neglecting the temperature dependency, for E_{LV} we have

$$\alpha = -\frac{k}{e} \left\{ \frac{b-1}{b+1} \left(\frac{E_{LV}}{2kT} + 2 \right) \right\}; \quad (16)$$

where α = differential thermal voltage,
 k = Boltzmann's constant,
 e = elementary charge,
 E_{LV} = energy difference between valence and conduction band,
 b = ratio μ_n/μ_p ,
 $\mu_{n,p}$ = mobility of electrons or holes,
 m^* = effective mass of the charge carrier,
 h = Planck's constant,
 n = carrier concentration.

With

$$\sigma = ne(\mu_n + \mu_p)$$

and

$$n = \frac{2 (2 \pi m^* k T)^{3/2}}{h^3} \exp(-E_{LV}/2 k T)$$

there is found

$$\mu_p = \frac{\sigma}{e n (b+1)}, \quad \mu_n = b \mu_p. \quad (17)$$

TABLE 5. CHARGE CARRIER MOBILITY IN POLYCYCLIC AROMATICS
(ACCORDING TO MANY, HARNIK AND GERLICH REF. 135)

Material	Thermal excitation energy (eV)	Calculated mobility (cm ² /Vs)	Reference
Cyananthrone	0.10	10 ⁻⁸	[137]
Indanthrone black	0.28	10 ⁻¹¹	
Indanthrone	0.32	10 ⁻¹²	
Indanthrazine	0.33	10 ⁻¹²	
Flavanthrone	0.35	10 ⁻⁷	
Isoviolanthrone	0.38	10 ⁻⁶	[136]
Violanthrone	0.39	10 ⁻⁶	
Isoviolanthrene	0.41	10 ⁻⁹	
Violanthrene	0.42	10 ⁻⁹	
Pyranthrone	0.53	10 ⁻⁹	
Pyranthrene	0.54	10 ⁻¹⁰	[99]
Ovalene	0.56	10 ⁻⁸	
M-naphthodanthrene	0.60	10 ⁻¹¹	
M-naphthodanthrone	0.65	10 ⁻⁹	
Isodibenzanthrone	0.75	10 ⁻⁵	
Anthracene (single crystal)	0.82	10 ⁻²	[67]
Anthracene (powder)	0.83	10 ⁻⁴	[99]
Anthracene (film)	0.96	10 ⁻⁴	[138]
Naphthacene (film)	0.82	10 ⁻³	
Anthanthrene	0.84	10 ⁻⁷	[136]
Anthanthrone	0.85	10 ⁻⁶	
Pentacene (film)	0.86	10 ⁻²	[138]
Perylene (film)	0.97	10 ⁻²	
Coronene	1.15	10 ⁻³	[99]
Metal-free phthalocyanine	1.20	1	
Copper phthalocyanine	1.30	10	
5,6(N)-pyridino-1,9-benzanthrone	1.60	10 ²	
Hydroviolanthrene	1.70	10 ²	
Naphthalene (single crystal)	1.85	(10 ¹¹)	[106]

With p conduction, α is

$$\alpha = + \frac{k}{e} \left\{ 2 + \ln \left[2 \left(\frac{2 \pi m_p^* k T}{h^2} \right)^{3/2} \right] - \ln n_p \right\} \quad (18)$$

and with mixed conduction

/515

$$\alpha = - \frac{k}{e} \frac{1}{b n_n + n_p} \left\{ 2 (b n_n - n_p) - b n_n \left(\ln n_n - \ln \left[2 \left(\frac{2 \pi m_n^* k T}{h^2} \right)^{3/2} \right] \right) + \right. \\ \left. + n_p \left(\ln n_p - \ln \left[2 \left(\frac{2 \pi m_p^* k T}{h^2} \right)^{3/2} \right] \right) \right\} \quad (19)$$

Pohl and Engelhardt (ref. 33) use equations (17) and (18) for the measurement of the Seebeck coefficients of various polyacene quinone radical polymers and obtain for the mobility ratio values of 0.47 to 1.04 in the case of intrinsic conduction and the mobilities presented in table 6. The temperature dependence of the differential voltage $|d\alpha/dT|$ lies in the range of a few $\mu V/\text{degree}$. /516

The extrinsic conduction model leads to impurity concentrations of 10^{24} cm^{-3} and is not applicable here. Hamann and Starke (ref. 84) find, in application of (16) and (17) to thermal voltage measurements, modifications of the mobility ratio of metal free phthalocyanine from 0.35 to 1.07 (table 6), but they were unable to show any temperature dependence of the Seebeck coefficients.

Slough (ref. 107) obtains an increasing carrier concentration for polyvinyl-naphthalene complexes if the acceptor content increases, whereby simultaneously the carrier mobility decreases (table 6). He concludes that there is increasing trapping of charge carriers in the acceptor molecule. The use of weaker acceptors (chloranil) increases mobility. Almost without exception polymers, heterocyclics and complexes present a positive differential thermal voltage. If the results are interpreted in the light of the model of an intrinsic conductor, there are mobilities for holes that are up to triple those of electrons. The absolute values thus found for mobilities are often below the present limit for detection of the Hall effect. Sehr et al. (ref. 78) find a temperature dependence of the Seebeck coefficient ($-60 \dots + 300^\circ \text{ C}$) for 3,8-diaminopyrene chloranil, with an increase in proportion to the rise in temperature and exceeding of a maximum (fig. 21).

The scant number of Hall effect measurements thus far available cannot give a complete picture. The most valuable data on charge transport are to be anticipated from these studies however. Epstein and Wildi (ref. 35) measure the Hall effect of pyrolyzed poly copper phthalocyanine in the temperature range of 25° to 450° C . The Hall voltages are proportional to the magnetic field

($\approx 4000 \text{ G}$) and current density ($\approx 8 \times 10^{-2} \text{ A/cm}^2$).

TABLE 6. CONCENTRATION AND MOBILITY OF CHARGE CARRIERS IN ORGANIC SEMICONDUCTORS AT ROOM TEMPERATURE

Material	μ_n (cm ² /Vs)	μ_p (cm ² /Vs)	n_n (cm ⁻³)	n_p (cm ⁻³)	Reference
Mobility from thermoelectric measurements					
Polyacene quinone radical polymers (PAQR) with:					
Dibenzpyrene	0.41	0.39	$8.3 \cdot 10^{15}$	$= n_n$	[33]
Pyrene (306° C)	$6.2 \cdot 10^{-3}$	$7.5 \cdot 10^{-3}$	$6.0 \cdot 10^{16}$	$= n_n$	
Pyrene (253° C)	$1.7 \cdot 10^{-2}$	$1.8 \cdot 10^{-2}$	$1.1 \cdot 10^{16}$	$= n_n$	
Phenanthrene	$3.1 \cdot 10^{-3}$	$4.5 \cdot 10^{-3}$	$8.3 \cdot 10^{15}$	$= n_n$	
Anthracene	$2.1 \cdot 10^{-3}$	$4.3 \cdot 10^{-3}$	$1.2 \cdot 10^{15}$	$= n_n$	
Metal-free phthalocyanine:					
α-Modification	66	160	$2.8 \cdot 10^6$	$= n_n$	[84]
α-Modification (sublimated)	0.074	0.19	$1.2 \cdot 10^8$	$= n_n$	
β, α-Modification	$3.1 \cdot 10^{-5}$	$2.9 \cdot 10^{-5}$	$5.2 \cdot 10^9$	$= n_n$	
β-Modification	0.18	0.18	$1.6 \cdot 10^3$	$= n_n$	
β-Modification (ground)	0.19	0.53	$3.5 \cdot 10^5$	$= n_n$	
γ-Modification	13	26	$1.6 \cdot 10^7$	$= n_n$	
Polyvinyl naphthalene complex with:					
Tetracyanoethylene	-	10^{-6}	-	10^{15}	[107]
1/2 (Tetracyanoethylene)	-	10^{-2}	-	10^{12}	
Chloranil	-	10	-	10^8	
Hall mobilities					
Poly-copper-phthalocyanine	-	2.5	$= n_p$	10^{18}	[35]
Metal-free phthalocyanine, β-Modification	0.1...0.4	-	$(2...12) \cdot 10^6$	-	[37]
Copper phthalocyanine, β-Modification	-	215*)	-	10^8 *)	[38]
Copper phthalocyanine, β-Modification	88	131	-	-	[39]

*) Measuring temperature 137° C.

TABLE 6. CONTINUED

Material	μ_n (cm ² /Vs)	μ_p (cm ² /Vs)	n_n (cm ⁻³)	n_p (cm ⁻³)	Reference
Mobilities from photoelectric measurements					
Anthracene single crystals					
to c-axis	0.54 ± 0.03	0.98 ± 0.04	-	-	[41]
		2.3	-	-	[69]
⊥ to ab-plane	0.3	0.4	-	-	}
to ab-plane	2.0	1.3	-	-	
p-Terphenyl	-	$2.5 \cdot 10^{-2}$	-	10^4	[140]

For pyrolysates thermally heated up to 350° C the Hall coefficient is pronouncedly temperature dependent, which phenomenon must be attributed to the degassing of the product in vacuum. Products pyrolyzed at 450° C show a temperature constant Hall coefficient of 10^3 cm³/As.

In intrinsic conduction, for nondegeneration of the energy bands as /518 well as for privileged scatter through single phonon processes (purely thermal scatter)

$$R = -\frac{3\pi}{8} \frac{1}{e n} \frac{\mu_n - \mu_p}{\mu_n + \mu_p}, \quad (20)$$

is valid, whereby R is obtained from

$$R = \frac{E_y}{i_x H_z}$$

where E_y = field strength on the Hall probes,

H_z = magnetic field strength,

i_x = current through the Hall probe.

For excess (21) or deficiency (22) conduction there is found

$$R = -\frac{3}{8} \pi \frac{1}{e n_n}, \quad (21)$$

$$R = + \frac{3}{8} \pi \frac{1}{e n_p} \quad (22)$$

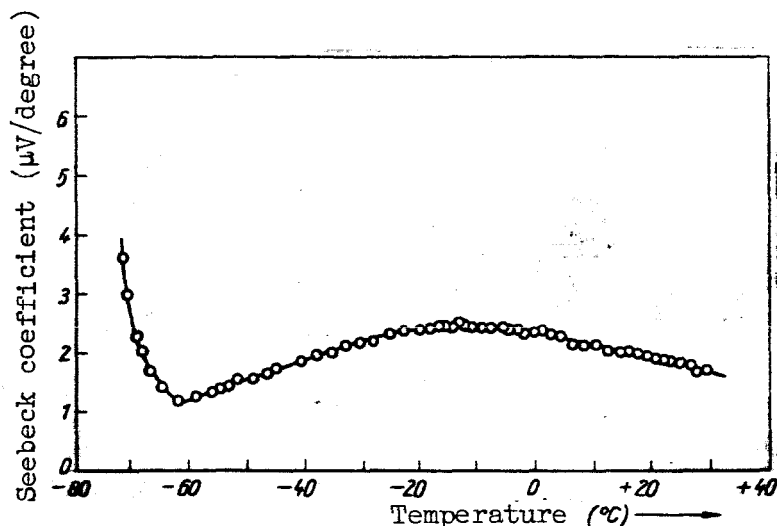


Figure 21. Temperature dependence of the Seebeck coefficient of 3,8-diaminopyrene chloranil (according to Sehr et al., ref. 78).

The value calculated according to (20) with $\mu_p \gg \mu_n$ is presented in table 6.

Delacote and Schott (ref. 38) obtain a temperature dependence of carrier mobility

from Hall effect measurements on copper phthalocyanine. Heilmeyer and Harrison (ref. 39) measure Hall mobility of copper phthalocyanine single crystals in magnetic fields of 6500 G. They find a reversal of the negative sign of the Hall voltage at 373° K. At the same time a break is observed in the temperature dependence of conductivity. This behavior can be interpreted through donor terms of 1.6 eV below the conduction band or acceptor terms of 1.6 eV above the valence band ($E_{LV} = 2$ eV). The defects are induced by oxygen.

Ohmically, polycyclic aromatics are especially high. Hall effect and thermal voltage experiments are not known thus far. Mobilities have been measured in anthracene (refs. 40, 41, 69 and 139) according to the capacitor method (cf. 7.5). Photoinduced carriers are formed in a superficial layer of 10 μm and move like electrons and holes in the electric field. The mobilities of both kinds of carriers are temperature dependent (see fig. 22) and anisotropic (table 6).

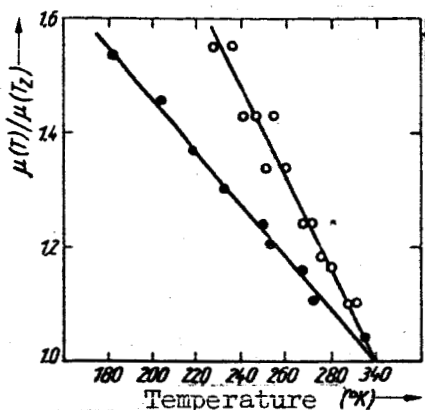


Figure 22. Temperature dependence of mobilities of electrons and holes in anthracene. Measurement on a single crystal \perp to the ab-plane (according to Kepler, ref. 40). ○, Electrons; ●, Holes.

8.4 Trap concentration and trap depth

/519

In organic molecular crystals of p type, holes can be injected through an ohmic anode. For anthracene, p-terphenyl and p-quaterphenyl, Mark and Helfrich (ref. 140) use the electrolyte-electrodes of Kallmann and Pope (refs. 104 and 141). In special cases the transfer of an electron from the valence band of the aromatic to the iodine is bound with an energy gain. For a trap-free crystal the transition from a current density i_Ω which obeys Ohm's law, to $\mu(T) < \sim T$

space charge-limited current density i_R occurs at $V_{\Omega R}$, $n_p \approx n_{op}$. The following are valid

$$V_{\Omega R} \approx n_{op} e d^2 / 2 \epsilon \epsilon_0, \quad (23)$$

$$i_\Omega = e \mu_p n_{op} V/d, \quad (24)$$

$$i_R = \frac{9}{8} \mu_p \epsilon \epsilon_0 V^2/d^3; \quad (25)$$

where n_{op} = concentration of holes in thermal equilibrium,

n_p = concentration of injected holes,

$V_{\Omega R}$ = transition voltage,

e = elementary charge,

ϵ = (relative) dielectric constant,

ϵ_0 = influence constant,

d = electrode distance,

μ_p = hole mobility,

V = applied voltage,

H = trap concentration.

For molecular crystals with traps, equations are valid that are presented in reference 140. The current density i_H here is

$$i_H \sim V^{l+1}, \quad l = \frac{T_c}{T} > 1$$

(T_c characterizes the trap distribution, T = temperature in degrees K).

For $n_{op} < n_p < n_H$ it is found that in this area absolute values and voltage dependence of the current through trap concentration and distribution can be determined. A second transition in the case $n_p \approx n_H$ is found, i.e., all traps are occupied. Here i_H again joins i_R . This transition is found at a voltage V_{HR} (fig. 23):

$$V_{HR} \approx \frac{e d^2}{\epsilon \epsilon_0} \left[\frac{9 H^l}{8 N_0} \left(\frac{l+1}{l} \right)^l \left(\frac{l+1}{2l+1} \right)^{l+1} \right]^{\frac{1}{l-1}} \quad (26)$$

N_0 , effective state density in the valence band. V_{HR} for $l \rightarrow \infty$ (equivalent with a uniform distribution of trapped space charge in the crystal volume) is converted to (ref. 142)

$$V_{HR} \approx e H d^2 / \epsilon \epsilon_0 \quad (27)$$

Using the above equations, and from measurements of the current-voltage characteristic, and analysis of the deformation of square-wave voltage pulses

on passage through the crystal, trap concentrations of 10^{13} cm^{-3} were found for anthracene and p-terphenyl. The quasi Fermi level, i.e., the highest occupied trap level at T = 0, is 0.45 eV for p-terphenyl (test voltage 80 V) and 0.71 eV for anthracene (test voltage 74 V) over the uppermost edge of the valence band (ref. 140).

Heilmeyer and Warfield (ref. 143) measure the current-voltage characteristic of single crystals of metal free phthalocyanine. The ohmic behavior is evident for the dark current i_D of 15 to 10^4 V. Above this range current $i_D \sim V^2$. The photocurrent is proportional to the voltage to $3.6 \cdot 10^4$ V/cm (limit of

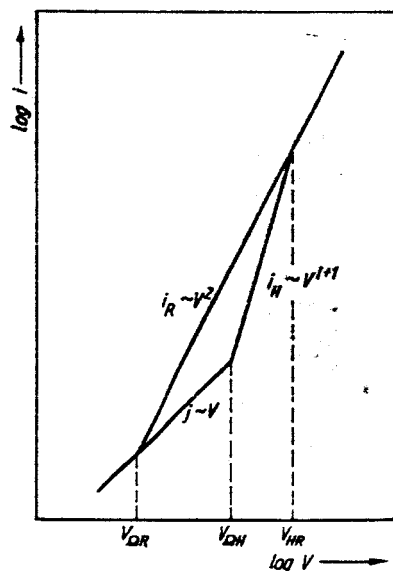


Figure 23. Complete current voltage characteristic of space charge-limited currents (according to Mark and Helfrich ref. 140).

measurement), which is an indication of a carrier mobility that is independent of field strength. The measurement, according to equations (23) to (27) shows trap concentrations of 10^{12} to 10^{14} cm^{-3} , a concentration of free charge carriers of 10^6 to 10^7 cm^{-3} , and a trap depth of 0.8 eV below the conduction band. This scanty trap concentration in the organic molecular crystal is inconsistent with similar values in much purer inorganic crystals. Metallic impurities of the order of magnitude 0.1 percent appear to be neither the basis for traps nor charge carrier sources.

Devaux, Schott and Lazerges (ref. 144) determine the intensity dependence of photocurrents in copper phthalocyanine single crystals. They find at the surface $i_{ph} \sim \sqrt{I}$ (I = light intensity) and deduce from this the existence of traps between the valence band and the Fermi level. With the applied voltage i_{ph} varies as $V^{1.5}$. Gray gives the equation for temperature dependence of space charge-limited currents (ref. 145).

8.5 The anisotropy of the electric conductivity

The anisotropy of transport magnitudes of organic molecular crystals was determined in only a few cases heretofore. The measured values available

TABLE 7. ANISOTROPY OF ELECTRIC CONDUCTIVITY

Material	Measured value	x-Axis	y-Axis	z-Axis	Polycrystalline	Reference
Diaminodurene chloranil	$\rho_{250^\circ\text{C}} (\Omega \text{ cm})$	$7.0 \cdot 10^4$	$6.9 \cdot 10^4$	$8.4 \cdot 10^4$	$3.0 \cdot 10^4$	[79]
	$E (\text{eV})$	0.26	-	-	0.29	
	$S_{300^\circ\text{C}} (\mu\text{V}/\text{deg})$ $S_{-500^\circ\text{C}} (\mu\text{V}/\text{deg})$	300 300	- -	- -	300 130	
1,5-diaminodurene chloranil	$\rho_{250^\circ\text{C}} (\Omega \text{ cm})$	$1.3 \cdot 10^9$	$6.3 \cdot 10^{11}$	$2.0 \cdot 10^{11}$	$7.2 \cdot 10^{11}$	[79]
	$E (\text{eV})$	0.60	0.74	0.74	0.65	
$[(\text{C}_2\text{H}_5)_3\text{NH}]^+[\text{TCNQ}]^-[\text{TCNQ}]^0$	$\sigma (\Omega \text{ cm})^{-1}$	Main axis of crystal			-	[29]
		4.0	0.05	0.001		

TABLE 8. COMPARISON OF CONCENTRATION OF UNPAIRED ELECTRON SPINS AND CHARGE CARRIER CONCENTRATION (ACCORDING TO SEHR, LABES ET AL, REF. 78)

Material	Composition A:B	Unpaired spins/mol	Unpaired spins/molecule	Conductivity at 300° K ($\Omega \text{ cm})^{-1}$	Charge carrier concentration (cm^{-3})
p-phenylene diamine chloranil	3:2	7	0.01	$1.7 \cdot 10^{-7}$	10^{15}
p-phenylene diamine bromanil	3:1	2.1	0.03	$5 \cdot 10^{-11}$	$3 \cdot 10^{11}$
p-phenylene diamine iodanil	3:2	1.7	0.02	$7 \cdot 10^{-11}$	$5 \cdot 10^{11}$
3,8-diaminopyrene chloranil	1:1	3	0.004	$2 \cdot 10^{-4}$	$2 \cdot 10^{18}$
3,8-diaminopyrene bromanil	1:1	9	0.01	$1 \cdot 10^{-3}$	$6 \cdot 10^{18}$
3,8-diaminopyrene iodanil	1:1	≈ 0	≈ 0	$5 \cdot 10^{-7}$	$3 \cdot 10^{15}$
3,10-diaminopyrene chloranil	3:1	1.12	0.20	$2 \cdot 10^{-7}$	10^{15}
Perylene I2	1:3	1.7	0.03	$3 \cdot 10^{-1}$	$2 \cdot 10^{21}$
Coronene I2	1:1	≈ 0	≈ 0	$5 \cdot 10^{-9}$	$3 \cdot 10^{13}$

often show significant direction-dependence which can be qualitatively explained by crystal structure.

Kronick and Labes (ref. 79) measure the conductivity of diaminodurene chloranil (1:1 complex) in three directions (X, Y, Z) which are perpendicular to each other. The crystals had the form of needles or thin plates. Since the crystallographic data were not yet determined, the correlation of the X-, Y-, Z-axes to the crystal axes was not possible. The measuring method is shown in table 7. A stronger anisotropy was found for 1,5-diaminonaphthalene chloranil. The anisotropy of the Seebeck coefficient can be estimated from the comparison of the measured values of single crystals and polycrystalline material. Kepler, Bierstedt and Merrieffield (ref. 29) find a pronounced anisotropy of conductivity and an isotropic excitation energy for the tetra cyanoquinone dimethane complex $[(C_2H_5)_3NH]^+ [TCNQ]^- [TCNQ]^0$. Mette and Pick (ref. 67) give

an isotropic conductivity for anthracene crystals in the ab plane at 118° C with a deviation < 10 percent of a median value. Perpendicular to the ab plane, the conductivity is lower by one order of magnitude. In naphthalene single crystals there is conduction in the ab plane which is higher by only a factor of 2, compared to that in a direction perpendicular thereto (ref. 106). Kepler (ref. 40) finds a slight anisotropy of mobility of the charge carrier for anthracene, also in the ab plane. Perpendicular and parallel to the ab plane there was a reversal of the ratio of mobility of electrons and holes (see table 6). /522

8.6 Concentration of unpaired spins

Even at an early stage of the study of organic semiconductor compounds, significant concentrations of unpaired electron spins were observed in these substances by measurements of paramagnetic electron resonance (PER). The resonance lines of a few oersteds width are near a g factor of 2.0036, which value is an indication of displaced electrons. In the meantime there have been many studies in this field (refs. 29, 33, 56, 64, 78, 101, and 146-158). It was the object of many measurements to find a correlation between conductivity or charge carrier concentration and spin concentration. Where the possibility

of comparison existed, spin concentrations in the range of 10^{17} to 10^{23} g^{-1} exceed charge carrier concentration by many orders of magnitude. Charge carriers and spin concentration are temperature dependent for the most part in different ways. Nevertheless there is a correlation between spin concentration and conductivity in some cases.

Sehr, Labes et al. (ref. 78) were able to show for molecular complexes that the concentration of spins and charge carriers is unrelated (table 8). The charge carrier concentration was calculated from the conductivity by the

assumption of a charge carrier mobility of $10^{-3} \text{ cm}^2/\text{Vs}$. Only every 5th to 100th molecule carries an unpaired electron. In this connection the relatively low conductivity of α, α -diphenyl- β -picryl hydrazyl with one unpaired electron per molecule is characteristic. Unpaired spins in molecular complexes are

considered to be the basis of bonding with strong ion components. The narrow lines are evidence of a strong exchange effect. The concentrations in question are of the same order of magnitude only for the perylene-iodine complex.

Singer and Kommandeur (ref. 150) find in the case of the pyrene-iodine complex that the concentration of unpaired spins and the conductivity have an exponential temperature dependence with approximately the same excitation energy. At lower temperatures the spin concentration is constant, which is an indication of trapping of electrons.

Berlin et al. (refs. 55 to 59) indicate unpaired spins of 10^{17} to 10^{19} g⁻¹ for polymer concentrations. The narrow PER signal also occurs in dissolved

polymers. For one unpaired electron there are 10 to 10^5 molecules. With collective exchange of unpaired electrons in conjugated polymers, there is a broad signal (500 to 1000 Oe) in addition to narrow lines. The unpaired electrons are taken by Berlin to be biradicals which are seated on especially large polymer molecules. With thermal treatment the number of such molecules is increased by polymerization (ref. 4b).

8.7 Catalytic properties

523

Organic semiconductors have catalytic properties. The first studies showed that high catalytic activity can be achieved, similar to that of inorganic semiconductor catalysts. It has been known for a long time that hemin and its complexes can have a catalytic effect. Cook studied phthalocyanine in this connection (ref. 159) as early as 1938. Polymers have recently been brought into the picture. Topchiev (refs. 112 and 162) points out that organic semiconductor catalysts open up new possibilities of heterogeneous catalysis. They are distinguished from inorganic catalysts in that they have selective activity. It can thus be shown that pyrolyzed polyacrylonitrile decomposes hydrogen peroxide, hydrazine hydrate and formic acid, but is completely inactive with respect to alcohols.

Nesmeyanov et al. (ref. 16) obtain semiconducting polymers by dehydrochlorination of methylβchlorvinyl ketones. These products have high catalytic activity for the oxidation of toluene. The activity is three times as great as that of active charcoal.

8.8 Molecular substitution lattice defects

As shown in section 6.3, it is possible to dope organic molecular crystals of a high degree of purity. The effect of the doping upon electric and photoelectric properties excites lively interest (refs. 53, 97, and 163-166). Northrop and Simpson (ref. 53) dissolve naphthacene, pentacene, perylene and anthanthrene in a mol ratio of 1:1000 in highly purified anthracene, pyrene or chrysene. At high temperatures the thermal excitation energies of the pure base substance are found, and at low temperatures an excitation energy appears whose value is determined only by the type of impurity, and not by its concentration. The position of the transition from extrinsic to intrinsic conduction

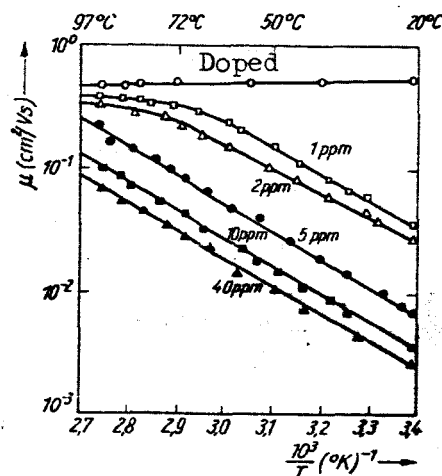


Figure 24. Effect of naphthacene doping on mobility of the charge carrier in anthracene (according to Hoesterey and Letson, ref. 163).

in the $\log \sigma \cdot 1/T$ diagram is dependent upon concentration. Hoesterey and Letson (ref. 163) investigated the formation of traps by anthraquinone, anthrone and naphthacene in zone-refined anthracene.

Naphthacene acts as an impurity trap 0.43 eV above the valence band with a trap cross section $> 10^{-15} \text{ cm}^2$. Figure 24 illustrates how the charge mobilities determined according to the capacitor method vary as a function of concentration in a solid solution of naphthacene in anthracene. Akamatu and Inokuchi (ref. 164) describe measurements on a violanthrene iodine 2 complex, the conductivity of which is strongly dependent upon the iodine content and which passes through a maximum at a (1:1) composition. By doping with iodine, tetracyanoethylene or chloranil (3.5×10^{-5} mol percent) the dark current of violanthrene is increased by 3 to 6 orders of magnitude (ref. 166). In magnesium-phthalocyanine, according to Putseiko (ref. 97) electron traps develop through addition of electron acceptors. Quinone increases the photosensitivity of amorphous and microcrystalline Mg-Pc by two or three orders of magnitude.

8.9 Adsorbed gases and vapors

Gases and vapors affect dark and photoconduction at the surface of organic semiconductor compounds. The systematic investigation of this effect contributes substantially to the understanding of the mechanism of conduction (refs. 25, 106, 125 and 167-178).

Compton, Schneider and Waddington (refs. 170 and 173) studied the effect of various gases and vapors on the photo and dark conductivity of anthracene. The acceptors Cl_2 and NO_2 increase the photo and dark currents but lead to

TABLE 9. THERMAL EXCITATION ENERGY (IN eV) OF SOLID SOLUTIONS
(ACCORDING TO NORTHROP AND SIMPSON, ref. 53).

Basic material	Impurity			
	Naphthacene	Pentacene	Perylene	Anthanthrene
Anthracene	1.23	0.95	1.58	1.12
Pyrene	1.25	1.03	1.61	1.16
Chrysene	1.26	1.02	1.57	1.16

chemical reactions with the molecular crystal. BF_3 , HCl , SO_2 , NO , O_2 are reversibly adsorbed and act in the same way. Donors NH_3 , $(\text{CH}_3)_3\text{N}$, $(\text{C}_2\text{H}_5)_2\text{O}$, $\text{C}_2\text{H}_5\text{OH}$, H_2O lower photoconductivity reversibly. CO_2 , N_2 , Ar , $(\text{CH}_3)_4\text{C}$ are inert.

Naphthalene becomes extrinsically conductive through the effect of O_2 adsorption, with a thermal excitation energy of 1.5 eV (intrinsic conduction value 3.6 eV) (ref. 106). Oxygen is not dissolved in naphthalene even at a partial pressure of 1 atm, but becomes localized inhomogeneously at lattice defects (ref. 172). Copper phthalocyanine single crystals behave quite differently, their surface photoconductivity being increased by the effect of a 1 atm oxygen pressure to only 1.12 to 1.16 times the value obtained at 10^{-6} Torr high vacuum (ref. 144).

Kuroda and Flood showed that m-dinaphthanthrene which has an excitation energy of 0.74 eV in the intrinsic conduction range becomes extrinsically conducting with 0.40 eV by the effect of oxygen. The m-dinaphanthrene which contains two oxygen atoms extends its intrinsic conductive range under oxygen to lower temperatures (ref. 177). While copper phthalocyanine in iodine vapor

reversibly changes its resistance from $1 \cdot 10^{14}$ to $4 \cdot 10^6 \Omega$ in a saturated bromine atmosphere there occurs a chemical reaction which leads to a decomposition of the Cu-Pc single crystal, as is the case under KCl_4I vapor (ref. 167). ⁵²⁵ Vartanyan (ref. 125) observed that oxygen increased the photoconduction of tryptaflavin. In the longwave region of the visible spectrum the effect is explained in terms of photosorption, while in the shortwave region photochemical reactions are also involved. Methylene blue (ref. 169) is converted to the reduced form (leukomethylene blue) when treated with hydrogen sulfide and water, the dark current of leukomethylene blue being much reduced in comparison to that of the starting substance. Reversals of the sign of the charge carrier are possible through the action of electronegative and electropositive gases. Through measurements under vacuum or inert gases, reproducible conditions can be established and environmental effects on the measured values can be eliminated.

9. Possible Applications of Organic Semiconductors

The above discussion has shown that there are convincing arguments in favor of the concept of organic semiconductors, but that for a valid explanation of conduction processes in organic solids further work must be done.

Building on the mathematical relationships so far worked out, first steps can be taken to find possible applications for organic semiconductor compounds.

9.1 Organic photodiodes and photocells

In publications and in the patent literature there is agreement on extraordinarily simple methods for the preparation of organic photodiodes and photocells (refs. 96, 124 and 179-185). Polycrystalline or amorphous organic semiconductors of p or n type and desired form can be produced by pressure processes, and brought into contact with an organic substance which because of its donor or acceptor properties leads to the formation of a barrier layer. Also it is possible to form p-n transitions by doping a base solid of uniform chemical structure. The characteristic magnitudes of such devices, such as no-load voltage, short circuit current or maximum delivered output are not yet adequate for technical purposes.

Kostelec (ref. 184) prepares thin polycrystalline layers of phthalene and triphenyl methane dyes and contacts with conductive glass. If the photocell is illuminated by a 100 watt tungsten lamp 10 cm away from the dye surface, there is a no-load voltage $U_0 = 100$ mV over the layer. There is a short-circuit cur-

rent of $i_0 = 0.5 \cdot 10^{-9}$ A/cm². The maximum output $N_{\max} = 6 \cdot 10^{-10}$ W. A barrier layer is formed between the dye and a surface layer, the thickness of which is determined by the absorption coefficient for the region of the spectrum used. Inokuchi, Maruyama and Akamatu (ref. 183) vaporize aromatics on an electrode and contact the free surface light-permeably with noble metals, zinc oxide or alkali metals. Upon illumination, photovoltages occur between the aromatic and the illuminated electrode (Noble metal contacts: $U_0 \leq 20$ mV, /526

$N_{\max} = 10^{-16}$ W, zinc oxide contact $U_0 = 20 \dots 450$ mV, alkali metal contacts $0.1 \dots 1$ V. $N_{\max} = 10^{-8} \dots 10^{-10}$ W). The relatively high no-load voltages for an alkali metal-aromatic combination can be explained on the basis of complex formation of an outer layer and the occurrence of a pn barrier layer.

Organic p-n layers also occur through the contact of merocyanines and triphenylmethane dyes (ref. 182). With a quantum yield of 10^{-2} , photocurrents $i_0 = 10^{-7}$ A occur which are free of inertia ($< 10^{-2}$ sec) and independent of electrode material. The p and n character of the dyes makes possible correct prediction of current direction. Between the dyes there is a balancing of the Fermi level, with development of a space discharge. In the electric field of

the surface layer the photo-induced pairs of electrons and holes are separated. Experiments with CdS-dye layers also afford an evaluation as p-n photocells, with a no-load voltage of 4 to 250 mV (refs. 180 and 181).

Wildi and Epstein (ref. 124) use 1 mm thick pressed layers of poly copper phthalocyanine which stoichiometrically presents a copper deficiency and which is n conductive. A p conducting surface layer is formed by copper excess or by the effect of oxygen, ozone, bromine, sulfur, selenium and tellurium.

Calvin and Kearns (refs. 96 and 179) patented a solar battery consisting of a pressed tablet of magnesium phthalocyanine and a layer of tetramethyl-p-phenylene diamine ($N_{\max} = 3 \cdot 10^{-12}$ W, $U_0 = 200$ mV).

9.2 Organic rectifiers

Up to the present, barrier effects have been found in only a few cases with semiconductors. Two methods were applied. In one case the p-n barrier layers are placed between organic semiconductors of differing types of conductivity. According to this method slight barrier effects were found between p and n conducting polyacrylonitrile (ref. 114) and for pressed-together layers of copper phthalocyanine and chlorine-indium chlorine-phthalocyanine (ref. 186). In the other case barrier layers can be built between organic semiconductors and metal contacts. Haak and Nolte (ref. 187) showed that polycrystalline β -phthalocyanine which was treated with a few drops of a polar solvent (H_2SO_4 , HNO_3) has barrier effects in an arrangement with two metal

contacts. In these devices the less noble metal is negative in the low resistance direction. Increase of temperature leads to a rapid deterioration of the barrier properties. Hamann (ref. 186) uses mixed crystals of the α -modification of metal-free phthalocyanine and copper phthalocyanine ($T = 300^\circ$ K,

$\rho = 4.8 \cdot 10^6 \Omega \text{ cm}$, $E = 0.66 \text{ eV}$, $\alpha = +580 \mu\text{V/degree}$) to prepare a rectifier. The polycrystalline material is pressed to tablets, provided on one side with a metal surface contact and contacted on the opposite smooth surface with metal points. The ratio of the low resistance current to inverse current is maximally 3000:1 (system Ag surface, Pc, Al points). In a simple diode cir-

cuit these devices act as rectifiers for alternating current up to 10^4 Hz. The limiting of the rectifier effect at high frequencies is to be attributed to the effect of a high parallel capacitance of the point rectifier.

9.3 Thermoelectric structural elements and other possibilities for use /527

In addition to the application as photocells and rectifiers in the low frequency ranges, it appears that ways will be sought to introduce organic semiconductors as thermoelectric structural elements (refs. 30, 35, 110 and 188). Polymers that are produced by reaction of pyromellitonitrile and hydrogen sulfide or methanol have a specific resistance to 2 to 1000 $\Omega \text{ cm}$, Seebeck coefficient $\alpha = -150$ to $+9 \mu\text{V/degree}$, and heat conductivity

$\lambda = 5 \cdot 10^{-3}$ to $1 \cdot 10^{-2}$ W/cm·degree. From these values there follow figures of merit of $4 \cdot 10^{-12}$ to $2 \cdot 10^{-8}$ (ref. 188).

The favorable spectral sensitivity of organic photoconductors (ref. 4) in UV, visible and IR can lead to their use as radiation detectors in specific spectral regions.

Other research concerning selective activities of organic semiconductor catalysts opens possibilities for synthesis of enzyme type catalysts.

10. The Importance of the Research Field and its Future

In the future, precision measurements of anisotropic transport magnitudes in molecular crystals will be needed which will permit confirmation of theoretical statements. The theory of charge transport in organic solids must be so built that conduction processes in partial crystals or amorphous materials can be completely included. Organic chemistry will be stimulated by the results already attained to develop new semiconducting organic substances, and so modify them that electrical characteristics will be obtained that maximally approximate the requirements of the physicist. Semiconductor organic polymers would be particularly valuable which would combine the outstanding mechanical and thermal properties (elasticity, thermoplasticity, low heat conductivity) of polymer insulators with the properties demanded of a semiconductor. Such substances could serve in the form of plates, sheets and filaments for the manufacture of photocells, thermoelectric structures (thermal batteries, cooling elements, thermo elements).

As has already been mentioned, the research results obtained on semiconductor properties of organic compounds are not limited to the field of investigation and application of organic semiconductors alone. The most substantial influences are in clarification of important life processes in the animal and plant organism. If it is possible to grasp the mechanism of highly selective catalytic reactions in the living organism, there will be many new impulses imparted to the catalysis of chemical reaction. It has been known for some time that substances contained in exhaust gases are carcinogenic or cancer stimulating. The carcinogenic compounds known thus far are either organic semiconductors or semiconductors are present in their structure, or they have a very similar structure.

Although of course there are no phthalocyanine or chlorophyll single crystals in living material, basic experiments on highly purified systems of known stereostructure must be performed. /528

Finally let me thank Dr. E. Rexer for encouraging this work and for his many valuable discussions. I thank Dr. L. Wuckel and the colleagues of the Organic Semiconductors Working Group in the Institute for Metal Physics and Pure Metals, Dresden, and Mrs. I. Storbeck, Mr. J. Heim and Mr. M. Stark for their criticism and comment.

REFERENCES

1. Hannay, N. B. Semiconductors, Reinhold Publ. Corp., New York, pp. 634-675, 1959.
2. Inokuchi, H. and Akamatu, H. Elektroprovodnost' organ. poluprovodnikov, Izdatel'stvo inostrannoy literatury, Moscow, 1963.
3. Gutman, F. and Netschey, A. Rev. Pure Appl. Chem, 12, 2, 1962.
4. Görlich, P. Photo Effects (Photoeffekt). Geest and Portig, Leipzig, Vol. 2, p. 243, 1963.
- 4a. Joffe, A. F. Physics of Semiconductors (Physik der Halbleiter). Akademie-Verlag, Berlin, p. 374, 1958.
- 4b. Topchev, A. V. Organic Semiconductors (Organicheskiye poluprovodniki). Izdatel'stvo Akademii Nauk SSSR, Moscow, 1963.
5. Pocchettino, A. Atti Accad. Lincei Rendiconti, 15, 355, 1906.
6. Königsberger, J. and Schilling, K. Ann. Phys., 32, 179, 1910.
7. Volmer, M. Ann. Phys., 40, 775, 1913.
8. Petrikaln, A. Z. Phys. Chem., 10, 9, 1930.
9. Suhrmann, R. Z. Phys., 94, 742, 1935.
10. Szent-Györgyi, A. Nature, 157, 875, 1946.
11. Terenin, A. Electrical Conductivity Symposium, Durham 1960, Intersci. Publ., p. 39, 1961.
12. Eley, D. D. Nature, 162, 819, 1948.
13. Vartanyan, A. T. Zh. Fiz. Khim., 22, 769, 1948.
14. McNeill, R. and Weiss, D. E. Austral. J. Chem., 12, 643, 1959.
15. Topchiev, A. V., Geiderich, M. A. et al. Dokl. Akad. Nauk SSSR, 128, 312, 1959.
16. Wassermann, A. Chem. Engng. News, 38, 46, 1960.
17. Talroze, V. A. and Blyumenfeld, A. A. Dokl. Akad. Nauk SSSR, 134, 1123; 135, 1450, 1960.
18. Geyderich, M. A., Davydov, B. E. et al. Mezhdunarodnyy Simposium po Makromolekulyarnoy Khimii, Moscow, Doklady i Avtoreferaty, p. 85, 1960.

19. Akamatu, H., Inokuchi, H. and Matsunaga, Y. *Nature*, 173, 168, 1954.
20. --- *Bull. Chem. Soc. Japan*, 29, 213, 1956.
21. Matsunaga, Y. *Bull. Chem. Soc. Japan*, 28, 475, 1955.
22. Kommandeur, J. and Hall, F. R. *Bull. Amer. Phys. Soc.*, 4, 421, 1959.
23. Uchida, T. and Akamatu, H. *Bull. Chem. Soc. Japan*, 34, 1015, 1961.
24. Davis, K. M. C., Eley, D. D. and Snart, R. S. *Nature*, 188, 724, 1960.
25. Snart, R. S. *Trans. Faraday Soc.*, 59, 754, 1963.
26. Rosenberg, B. *J. Chem. Phys.*, 34, 63, 1961.
27. Nelson, R. C. *J. Chem. Phys.*, 27, 864, 1957.
28. Terenin, A., Putseiko, E. and Akimov, J. *Disc. Faraday Soc.*, 27, 1763, 1959.
29. Kepler, R. G., Bierstedt, P. E. and Merrifield, R. E. *Phys. Rev. Letters*, 5, 503, 1960.
30. Labes, M. M., Sehr, R. and Bose, M. *J. Chem. Phys.*, 32, 1570, 1960.
31. Fielding, P. E. and Gutman, F. *J. Chem. Phys.*, 26, 411, 1957.
32. Nelson, R. C. *J. Chem. Phys.*, 22, 890, 1954.
33. Pohl, H. A. and Engelhardt, E. H. *J. Phys. Chem.*, 66, 2085, 1962.
34. Hamann, C. and Storbeck, I. *Naturwissenschaften*, 50, 327, 1963.
35. Epstein, A. and Wildi, B. / *Electrical Conductivity Symposium*, 1960, Intersci. Publ., p. 337, 1961.
36. --- *J. Chem. Phys.*, 32, 324, 1960.
37. Heilmeyer, G. H., Warfield, G. and Harrison, S. E. *Phys. Rev. Letters*, 8, 309, 1962.
38. Delacote, G. and Schott, M. *Phys. Stat. Sol.*, 2, 1460, 1962.
39. Heilmeyer, H. and Harrison, S. E. *Phys. Rev.*, 132, 2010, 1963.
40. Kepler, R. G. *Phys. Rev.*, 119, 1226, 1963.
41. le Blanc, Jr., O. H. *J. Chem. Phys.*, 33, 626, 1960.
42. Landoldt-Börnstein, Springer-Verlag, Berlin, Vol. I, 4, p. 300, 1955.

43. Holzmüller, W. and Altenburg, K. Physics of Synthetic Materials (Physik der Kunststoffe). Akademie-Verlag, Berlin, p. 265, 1961.
44. Bayliss, N. S. J. Chem. Phys., 16, 287, 1948.
45. Kuhn, H. J. Chem. Phys., 16, 840, 1948.
46. Simpson, W. T. J. Chem. Phys., 16, 1124, 1948.
47. Staab, H. A. Introduction to Theoretical Organic Chemistry (Einführung in die Theoretische Organische Chemie). Verlag Chemie, Weinheim, 1959.
48. Eley, D. D. and Parfitt, G. D. Trans. Faraday Soc., 51, 1529, 1955.
49. Fröhlich, H. and Sewell, G. L. Proc. Phys. Soc., 74, 643, 1959.
50. Toyozawa, Y. J. Appl. Phys., 33, 340, 1962.
51. Riehl, N. Ann. Phys., 20, 93, 1955.
52. --- Zh. Fiz. Khim., 29, 959, 1955.
53. Northrop, D. C. and Simpson, O. Proc. Roy. Soc., London, 234, 124, 1956.
54. Winslow, F. H., Baker, W. O. and Yager, W. A. J. Amer. Chem. Soc., 77, 4751, 1955.
55. Berlin, A. A., Matveyeva, N. G. et al. Vysokomolekulyarnyye Soyedineniya, 4, 860, 1962.
56. Berlin, A. A. and Matveyeva, N. G. Dokl. Akad. Nauk SSSR, 140, 368, 1961.
57. Berlin, A. A. and Boguslavskiy, L. J. Dokl. Akad. Nauk SSSR, 136, 1127, 1961.
58. Levina, S. D., Lobanova, K. P., Berlin A. A. et al. Dokl. Akad. Nauk SSSR, 145, 602, 1962.
59. Berlin, A. A., Liogonkiy, B. I. and Parini, V. P. Mezhdunarodnyy Simposium po Makromolekulyarnoy Khimii, Moscow, Doklady i Avtoreferaty, p. 115, 1960.
- 59a. Storbeck, I. and Starke, M. Ber. Bunsenges. Phys. Chem., 69, 4, 343, 1965.
60. Marvel, C. S. and Rossweller, J. H. J. Amer. Chem. Soc., 80, 1197, 1958.
61. Marvel, C. S. and Martin, N. M. J. Amer. Chem. Soc., 80, 6600, 1958.
62. Davydov, B. E., Krencel, V. A., Popov, Yu. A. et al. Vysokomolekulyarnyye Soyedineniya, 5, 321, 1963.

63. Davydov, B. E., Popov, Yu. A. et al. *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 4, 759, 1963.
64. Beneš, M., Peška, J. and Wichterle, O. *Macromolecular Symposium, Paris*, 1963.
65. --- *Chem. Ind., London*, 562, 1962.
66. Eley, D. D. and Inokuchi, H. *Z. Elektrochem.*, 63, 29, 1959.
67. Mette, H. and Pick, H. *Z. Phys.*, 134, 566, 1952.
68. Kunze, J. Thesis, Faculty of Nuclear Technology, Technical University, Dresden, 1959.
69. Boroffka, H. *Z. Phys.*, 160, 93, 1960.
70. Sano, M. *Bull. Chem. Soc. Japan*, 34, 1668, 1961.
71. Kleiner mann, M., Azzaranga, L. and McGlynn, S. P. *J. Chem. Phys.*, 37, 1825, 1962.
72. Noddack, W., Meier, H. and Haus, A. *Z. Phys. Chem.*, 212, 55, 1959.
73. Vartanyan, A. T. *Zh. Fiz. Khim.*, 20, 1065, 1946.
74. Slough, W. and Ubbelohde, A. R. *J. Chem. Soc.*, 982, 1957.
75. Martin, G. C. and Ubbelohde, A. R. *J. Chem. Soc.*, 4948, 1961.
76. Holmes-Walker, W. A. and Ubbelohde, A. R. *J. Chem. Soc.*, 720, 1954.
77. Kommandeur, J. and Singer, L. S. *Electrical Conductivity Symposium, Durham, 1960, Intersci. Publ.*, p. 325, 1961.
78. Sehr, R., Labes, M., Bose, M. et al. *Electrical Conductivity Symposium, Durham, Intersci. Publ.*, p. 309, 1960.
79. Kronick, P. L. and Labes, M. L. *J. Chem. Phys.*, 35, 2016, 1961.
80. Labes, M., Sehr, R. and Bose, M. *J. Chem. Phys.*, 33, 868, 1960.
81. Linstead, R. P. and Lowe, A. R. *J. Chem. Soc.*, 1022, 1934.
82. Linstead, R. P. *Ber. dtsh. chem. Ges.*, 72, 93, 1939.
83. Liang, C. Y. and Scalco, E. G. *J. Electrochem. Soc.*, 110, 779, 1963.
84. Hamann, C. and Starke, M. *Phys. Stat. Sol.*, 4, 509, 1964.
85. Mainthia, S. B., Kronick, P. L. and Labes, M. M. *J. Chem. Phys.*, 37, 2509, 1962.

86. Wilke, K. Th. Crystal Growth Methods (Methoden der Kristallzüchtung). VEB Deutscher Verlag der Wissenschaften, Berlin, 1963.
87. Birks, I. B. Scintillation Counters, Pergamon Press, London, 1953.
88. Curran, S. C. Luminescence and the Scintillation Counter, Butterworth, London, 1953.
89. Sherwood, J. N. and Thomson, S. J. J. Sci. Instrum., 37, 242, 1960.
90. Lipset, F. R. Rev. Sci. Instrum., 29, 423, 1958.
91. Chadderton, L. T. J. Phys. Chem. Solids, 25, 731, 1963.
92. Bowden, P. F., Chadderton, F. R. S. and Chadderton, L. T. Proc. Roy. Soc., A 269, 143, 1962.
93. Honigmann, B. Z. Elektrochem., 58, 322, 1954.
94. Kommandeur, J., Korinek, G. J. and Schneider, W. G. Canad. J. Chem., 35, 998, 1957.
95. Henglein, A. and Schnabel, W. Angew. Chem., 74, 78, 1962.
96. Calvin, M. and Kearns, D. R. USP 3 057 947, 1962.
97. Putseiko, E. K. Dokl. Akad. Nauk SSSR, 148, 1125, 1963.
98. Bree, A., Carswell, O. J. and Lyons, L. E. J. Chem. Soc., 1728, 1955.
99. Eley, D. D., Parfitt, G. D. et al. Trans. Faraday Soc., 49, 79, 1953.
100. Bradley, R. S., Grace, J. D. and Munro, D. C. Trans. Faraday Soc., 58, 776, 1962.
101. Labes, M., Sehr, R. and Bose, M. Proc. Intern. Conf. on Semicond. Physics, Prague, 1960. Prague, Czech. Acad. Sci., p. 850, 1961.
102. Sano, M. and Akamatu, H. Bull. Chem. Soc. Japan, 34, 1569, 1961.
103. Kallmann, H. and Pope, M. Nature, 185, 753, 1960.
104. --- Nature, 186, 31, 1960.
105. Liang, C. J., Scalco, E. G. and Oneal, Jr., G. J. Chem. Phys., 37, 459, 1962.
106. Pick, H. and Wissman, W. Z. Phys., 138, 436, 1954.
107. Slough, W. Trans. Faraday Soc., 58, 2360, 1962.
108. Cardew, M. H. and Eley, D. D. Disc. Faraday Soc., 27, 115, 1959.

109. Voitenko, R. M. and Raskina, E. M. Dokl. Akad. Nauk SSSR, 136, 1137, 1961.
110. Wildi, B. S. USP 3 046 322, 1962.
111. Northrop, D. C. and Simpson, O. Proc. Roy. Soc., A 244, 377, 1958.
112. Topchev, A. V. J. Polymer Sci., A 1, 591, 1963.
113. Bitjukov, V. D. Vestnik Akad. Nauk SSSR, 30, 99, 1960.
114. Ayrapetyants, A. V., Voitenko, R. M., Davydov, B. E. et al. Dokl. Akad. Nauk SSSR, 148, 605, 1963.
115. Petruzelia, N. and Nelson, R. C. J. Chem. Phys., 37, 3010, 1962.
116. Ayrapetyants, A. V. and Rozenshteyn, L. D. Organicheskiye poluprovodniki 4, Leningrad, Ser. Poluprovodniki, 1963.
117. Levina, S. D., Lobanova, K. P. and Plate, N. A. Dokl. Akad. Nauk SSSR, 132, 1140, 1960.
118. Gobrecht, H., Franke, K.-H., Niemeck, F. et al. Z. Angew. Phys., 13, 261, 1961.
119. Gobrecht, H., Tausend, A. and Clauss, G. Z. Phys., 176, 155, 1963.
120. Balabanov, E. I. and Frankevich, E. S. Vysokomolekulyarnyye Soyedineniya, 5, 1684, 1963.
121. Matejec, R. Photogr. Korresp., 97, 67, 1961.
122. van Cakenberghe, J. L. and Gilles, J. M. DAS 1 119 357, 1961.
123. Lawrence, E. O. and Beams, J. W. Phys. Rev., 32, 478, 1930.
124. Wildi, B. S. and Epstein, A. S. USP 3 009 981, 1961.
125. Vartanyan, A. T. Zh. Fiz. Khim., 24, 1361, 1950.
126. Putseyko, E. K. Dokl. Akad. Nauk, 59, 471, 1948.
127. Akimov, I. A. Dokl. Akad. Nauk, 128, 691, 1959.
128. Witol, I. K. Trudy Instituta Fiziki i Astronomii Akademii Nauk Est. SSR, 8, 175, 1958.
129. Bergmann, L. and Häusler, J. Z. Phys., 100, 50, 1936.
130. Meier, H. Z. Phys. Chem., 208, 325, 1957/58.

131. Riehl, N. Workshop of the Semiconductors Specialist Committee of DPG (Arbeitstagung des Fachausschusses "Halbleiter" der DPG). Munich, 1964.
132. Vartanyan, A. T. and Rozenshteyn, L. D. Dokl. Akad. Nauk SSSR, 124, 295, 1959.
133. Vartanyan, A. T. and Karpovich, I. A. Dokl. Akad. Nauk SSSR, 111, 561, 1956.
134. Terenin, A. N. Zh. Vsesoyuznogo Khimicheskogo Obshchestva, 5, 498, 1960.
135. Many, A., Harnik, E. and Gerlich, D. J. Chem. Phys., 23, 1733, 1955.
136. Inokuchi, H. Bull. Chem. Soc. Japan, 24, 222, 1951.
137. --- Bull. Chem. Soc. Japan, 25, 28, 1952.
138. Northrop, D. C. and Simpson, D. Proc. Phys. Soc., B 67, 892, 1954.
139. Kepler, R. G. Electrical Conductivity Symposium, Durham, 1960, Intersci. Publ., p. 77, 1961.
140. Mark, P. and Helfrich, W. J. Appl. Phys., 33, 205, 1962.
141. Kallmann, H. and Pope, M. J. Chem. Phys., 32, 300, 1960.
142. Lampert, M. A. Phys. Rev., 103, 1648, 1956.
143. Heilmeyer, G. H. and Warfield, G. J. Chem. Phys., 38, 163, 1963.
144. Devaux, P., Schott, M. and Lazerges, M. Phys. Stat. Sol., 4, 43, 1964.
145. Gray, E. Brit. J. Appl. Phys., 14, 374, 1963.
146. Eley, D. D. and Willis, H. R. Electrical Conductivity Symposium, Durham, 1960, Intersci. Publ., p. 257, 1961.
147. Akamatu, H., Mrozowski, S. and Wobschall, D. Proc. of the Third Conference on Carbon, Univ. of Buffalo, p. 135, 1957.
148. Sosin, S. L., Korshak, V. V., Vasnev, V. A. et al. Izv. Akad. Nauk SSSR, Otdel Khim. Nauk, 9, 1644, 1962.
149. Roberts, E. M. and Koski, W. S. J. Amer. Chem. Soc., 83, 1865, 1961.
150. Singer, L. S. and Kommandeur, J. J. Chem. Phys., 34, 133, 1961.
151. Pshenitsyna, G. M. and Shantarovich, P. S. Vysokomolekulyarnyye Soyedineniya, 5, 1228, 1963.

152. von der Hoek, J. A., Lupinski, J. H. and Oosterhoff, L. J. *Molecular Phys.*, 3, 299, 1960.
153. Ottenberg, A., Hoffmann, C. J. and Osiecki, J. *J. Chem. Phys.*, 38, 1898, 1963.
154. Melby, L. R., Harder, R. J. et al. *J. Am. Chem. Soc.*, 84, 3374, 1962.
155. Bennett, J. E. and Ingram, D. J. E. *Nature*, 175, 130, 1955.
156. Ingram, D. J. E. and Bennett, J. E. *Microwave and Radiofrequency Spectroscopy. A general discussion of the Faraday Society*, University Press, Aberdeen, p. 140, 1955.
157. Kuroda, H., Koboyashi, U. et al. *J. Chem., Phys.*, 36, 457, 1962.
158. Blomgren, G. E. and Kommandeur, J. *J. Chem. Phys.*, 35, 1636, 1961.
159. Cook, A. H. *J. Chem. Soc.*, 1761, 1774, 1845, 1938.
160. Brooks, J. D. *Austral. J. Chem.*, 14, 645, 1961.
161. Nesmeyanov, A. N., Rubinshteyn, A. M. et al. *Dokl. Akad. Nauk*, 135, 609, 1960.
162. Dokukina, E. S., Roginskiy, S. Z. et al. *Dokl. Akad. Nauk*, 137, 893, 1961.
163. Hoesterey, D. C. and Letson, G. M. *J. Phys. Chem. Solids*, 24, 1609, 1963.
164. Akamatu, H. and Inokuchi, H. *Electrical Conductivity Symposium, Durham, 1960, Intersci. Publ.*, 1961.
165. Meier, H. and Albrecht, W. *Z. Elektrochem.*, 66, 765, 1962.
166. Kearns, D. R. and Calvin, M. *J. Amer. Chem. Soc.*, 83, 2110, 1961.
167. Curry, J. and Cassidy, P. *J. Chem. Phys.*, 37, 2154, 1962.
168. Vartanyan, A. T. and Karpovich, I. A. *Zh. Fiz. Khim.*, 32, 178, 1958.
169. Vartanyan, A. T. *Zh. Fiz. Khim.*, 31, 1792, 1957.
170. Schneider, W. G. and Waddington, T. C. *J. Chem. Phys.*, 25, 358, 1956.
171. Vartanyan, A. T. *Zh. Fiz. Khim.*, 30, 424, 1956.
172. Riehl, N. *Electrical Conductivity Symposium, Intersci. Publ.*, p. 61, 1961.
173. Compton, D. M. J. and Waddington, T. C. *J. Chem. Phys.*, 25, 1075, 1956.

174. Bree, A. and Lyons, L. E. J. Chem. Soc., 5179, 1960.
175. Eley, D. D. and Spivey, D. J. Nature, 188, 724, 1960.
176. Vartanyan, A. T. and Rozenshteyn, L. D. Fiz. tverd. Tela, 3, 713, 1961.
177. Kuroda, H. and Flood, E. A. Canad. J. Chem., 39, 1475, 1961.
178. Putseyko, E. K. and Terenin, A. N. Zh. Fiz. Khim., 30, 1019, 1956.
179. Kearns, D. and Calvin, M. J. Chem. Phys., 29, 950, 1958.
180. Meier, H. and Albrecht, W. Ber. Bunsenges, Physik. Chem., 68, 64, 1964.
181. Nelson, R. C. J. Opt. Soc. Amer., 46, 13, 1956; 46, 1016, 1956.
182. Meier, H. and Haus, A. Angew. Chem., 72, 17, 1960.
183. Inokuchi, H., Mauiyama, Y. and Akamatu, H. Electrical Conductivity Symposium, Durham, 1960, Intersci. Publ., p. 69, 1961.
184. Kostelec, J. UPS 3 009 006, 1961.
185. Ubbelohde, A. R. DBP 1 034 272, 1958.
186. Hamann, C. Phys. Stat. Sol., 4, 97, 1964.
187. Haak, F. A. and Nolta, J. P. J. Chem. Phys., 38, 2648, 1963.
188. Katon, J. E. and Wildi, B. S. J. Chem. Phys., 40, 2977, 1964.
189. Golf, G. B. F. Brit. P. 804 911.
190. Little, W. A. Phys. Rev., 134, A 1416, 1964.

SUPPLEMENT TO THE BIBLIOGRAPHY

The supplement contains survey articles of the field from 1 January 1959 to 31 December 1964, as far as they were available at the time. The papers quoted in the present work are not repeated.

- Coblentz, A. Electronics, 30, 144, 1957.
- Bohrer, J. J. New York Acad. Sci., Sect. 2, 20, 5, 367, 1958.
- Brenner, W. Materials, 12, 1960.
- Bube, R. H. Photoconductivity of Solids, New York-London, p. 408, 1960.

- Chih, J. Hua Hsüeh Tung Pao, 1, 20, 1960.
- Wilk, M. Z. Elektrochem., 64, 930, 1960.
- Brophy, J. J. Phys. Today, 14, 40, 1961.
- Dunlap, W. C. J. chem. Educat., 38, 238, 1961.
- Krentsel, B. A. Wissenschaft u. Fortschritt, 12, 458, 1961.
- Becher, M. and Mark, F. Angew. Chem., 73, 637, 1961.
- Garrett, C. G. B. Proc. Conf. Semicond. Phys., Prague, 1960, Czech. Acad. Sci., p. 844, 1961.
- Anonym. Chem. Engng. News, 40, 86, 1962.
- Juster, N. J. J. chem. Educat., 40, 547, 1963.
- Traynard, Ph. Ref. Inst. Franç. Petrole Ann. Combust. Liquides, 18, 62, 1963.
- Neiman, R. R. and Johnson, R. E. Intern. Sci. Technology 1964, No. 29, pp. 68-79, 106.
- Sazhin, B. I. Electrical Conductivity of Polymers (Elektroprovodnost' polimerov). Izdatel'stvo Khimiya, Moscow, 1964.
- Okamoto, Y. and Brenner, W. N.Y., p. 185, 1964.
- Chojnacki, H. Wiadomości chem., 18, 91, 1964.
- Hatano, M. Kagaku to Kogyo, 17, 792, 1964.

(Received January 19, 1965)

Translated for the National Aeronautics and Space Administration by
John F. Holman and Co. Inc.